

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
20 March 2003 (20.03.2003)

PCT

(10) International Publication Number  
**WO 03/022739 A2**

(51) International Patent Classification<sup>7</sup>: **C01B 31/02**,  
B01J 19/08

(21) International Application Number: PCT/GB02/04049

(22) International Filing Date:  
6 September 2002 (06.09.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
0121558.1 6 September 2001 (06.09.2001) GB  
0121554.0 6 September 2001 (06.09.2001) GB  
0123491.3 29 September 2001 (29.09.2001) GB  
0123508.4 1 October 2001 (01.10.2001) GB

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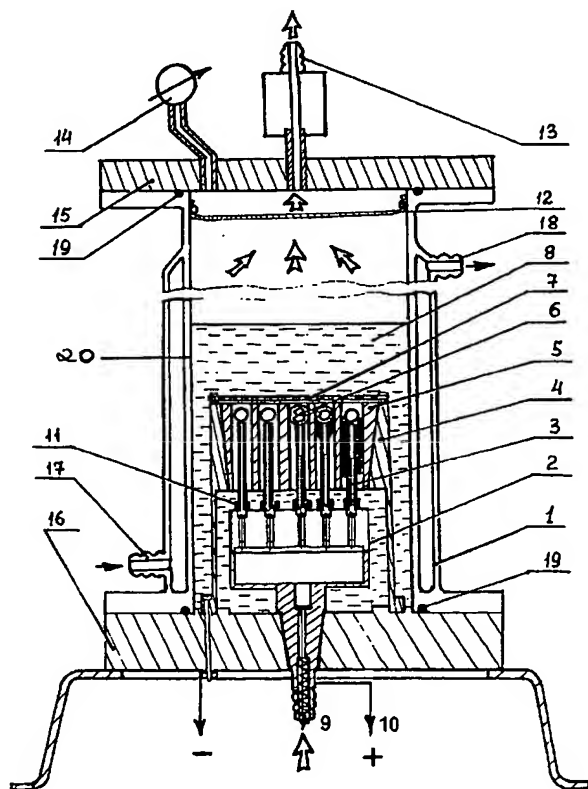
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(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,

[Continued on next page]

(54) Title: APPARATUS AND METHOD FOR NANOPARTICLE AND NANOTUBE PRODUCTION, AND USE THEREFOR  
FOR GAS STORAGE



(57) Abstract: There is provided a method for the enhanced production of fullerenes, nanotubes and nanoparticles. The method relies upon the provision of a hydrocarbon liquid which is converted by a suitable energy source to a synthesis gas such as acetone, ethylene, methane or carbon monoxide, the synthesis gas(es) forming the precursors need for fullerene, nanotube or nanoparticle production. The nanotubes formed by the method described are in general terms shorter and wider than conventionally produced nanotubes. An improved apparatus for production of the fullerenes and nanocarbons is also disclosed wherein a moveable contactor is attached to a first electrode with a sealable chamber, and is spaced from the second electrode such that an electric arc can pass between them.

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WO 03/022739 A2



GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

- (84) **Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK,

TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

- *without international search report and to be republished upon receipt of that report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

1     **Apparatus and Method for Nanoparticle and Nanotube**  
2     **Production, and Use Therefor for Gas Storage**

3  
4     The invention concerns the production of new carbon  
5     allotropes, namely, fullerenes, carbon nanotubes and  
6     nanoparticles (buckyonions), and also the  
7     encapsulation of such gases inside such nanocarbons  
8     (particularly nanotubes, nanohorns, nanofibers and  
9     other nanoporous carbons) for storage purposes.

10  
11    Carbon nanotubes are fullerene-like structures,  
12    which consist of cylinders closed at either end with  
13    caps containing pentagonal rings. Nanotubes were  
14    discovered in 1991 by Iijima [15] as being comprised  
15    of the material deposited in the cathode during the  
16    arc evaporation of graphite electrodes. Nanotubes  
17    have now been recognised as having desirable  
18    properties which can be utilised in the electronics  
19    industry, in material and strengthening, in research  
20    and in energy production (for example for hydrogen  
21    storage). However, production of nanotubes on a  
22    commercial scale still poses difficulties.

1 These allotropes are among the most desirable  
2 materials for basic research in both chemistry and  
3 physics, as well as applied research in electronics,  
4 non-linear optics, chemical technologies, medicine,  
5 and others.

6  
7 The processes of producing new allotrope forms of  
8 carbon, fullerenes, nanotubes and nanoparticles  
9 (buckyonions) are based on the generation of a cool  
10 plasma of carbon clusters by an ablation of carbon-  
11 containing substances, driven by lasers, ion or  
12 electron beams, a pyrolysis of hydrocarbons, an  
13 electric arc discharge, resistive or inductive  
14 heating, etc, and clusters' crystallization to the  
15 allotropes under certain conditions of annealing  
16 [1]. After which fullerenes are usually eluted from  
17 the soot by the use of aromatic solvents, such as  
18 benzene, toluene, xylenes, chlorobenzene, 1,2-  
19 dichlorobenzene, and the like [2]. Nanotubes on the  
20 other hand are separated from soot and buckyonions  
21 by the use of gaseous (air, oxygen, carbon oxides,  
22 water steam, etc) [3] or liquid oxidants (nitric,  
23 hydrochloric, sulfuric and other acids or their  
24 mixtures) [4].

25  
26 The processes of forming different carbon allotropes  
27 (for instance, fullerenes and nanotubes/buckyonions)  
28 are competitive and, therefore, it is possible to  
29 displace the balance in their output by changing  
30 conditions either of the generation process or of  
31 crystallization (annealing). In arc discharge  
32 processes, increasing the pressure of a buffer gas



1 (He or Ar) from 50 - 150 Torr, which is optimal for  
2 producing fullerenes, to 500 Torr leads to a  
3 preferential formation of Multi-Wall Nano Tubes  
4 (MWNT)/onions [5, 9]. Addition of some metal  
5 catalysts (Co, Ni, Pt, Fe, etc) to the initial  
6 graphite donor leads to preferential formation of  
7 Single-Wall NanoTubes (SWNT)[6] with a yield up to  
8 70% for laser ablation of the graphite. Despite  
9 outstanding results obtained with laser ablation  
10 [1], one can conclude that any process and apparatus  
11 based on laser ablation is not commercially viable  
12 because of the very low coefficient (few %) of  
13 transformation electric energy to energy deposited  
14 into vaporized targets.

15  
16 Processes for producing lower and higher fullerenes  
17 (that is, all fullerenes except  $C_{60}$  and  $C_{70}$ ) are less  
18 well developed than equivalent processes for  
19 producing the classical buckminsterfullerenes,  $C_{60}$   
20 and  $C_{70}$ . The main problem is a very low yield of the  
21 lower and higher fullerenes. For  $C_{74}$ ,  $C_{76}$ ,  $C_{78}$ , and  $C_{84}$   
22 the yield is usually about 1-3% and less than 0.1%  
23 for  $C_{90}$ ,  $C_{94}$ ,  $C_{98}$  in comparison to the yield of 0 -  
24 40% for the classical fullerenes [6]. For lower  
25 fullerenes, the yield is even lower. As a result,  
26 the amounts of such fullerenes available are too low  
27 to study their general properties.

28  
29 The existing methods and devices for producing  
30 fullerenes [7] suggests that graphite electrodes are  
31 placed in a contained volume filled by He gas at a  
32 pressure of 50 - 150 Torr. Under certain conditions

1 (electric current is up to 200 Å and voltage in the  
2 range 5-20 V), the graphite anode is evaporated and  
3 evaporated graphite clusters can form fullerene  
4 molecules, mainly C<sub>60</sub> (80-90%) and C<sub>70</sub> (~10-15%) as  
5 well as small amounts of higher fullerenes (total  
6 sum not exceeding 3 - 4%). High Performance Liquid  
7 Chromatography (HPLC) is then required to separate  
8 individual fullerenes [8].

9  
10 HPLC is characterised by a very low production of  
11 higher fullerenes and, as a result, market prices of  
12 the higher fullerenes are enormous, more than  
13 \$1,000-10,000 per gram. Higher order fullerene  
14 mixtures are produced by column chromatography in  
15 toluene, then are precipitated as a microcrystalline  
16 powder. The mixture contains varying amounts of C<sub>76</sub>  
17 through C<sub>96</sub>, but mainly C<sub>76</sub>, C<sub>78</sub>, C<sub>84</sub>, and C<sub>92</sub>.  
18 Therefore, usual inert gas arc methods are useless  
19 for producing higher fullerenes. Outputs of C<sub>76</sub>, C<sub>78</sub>,  
20 C<sub>84</sub> from such technologies are about a couple of  
21 milligrams a day per processor, whereas for lower  
22 fullerenes the outputs are even less.

23  
24 It is obvious that a preferential production of  
25 lower/higher fullerenes over classical ones, C<sub>60</sub> and  
26 C<sub>70</sub>, will help in solving the problem.

27  
28 Modak et al [10] occasionally produced a mixture of  
29 C<sub>60</sub> with hydrides of lower (C<sub>36</sub>, C<sub>40</sub>, C<sub>42</sub>, C<sub>44</sub>, C<sub>48</sub>, C<sub>50</sub>,  
30 C<sub>52</sub>, C<sub>54</sub>, C<sub>58</sub>) and higher (C<sub>72</sub>, C<sub>76</sub>) fullerenes by  
31 using a high-voltage AC arc-discharge in a liquid  
32 benzene and/or toluene medium. An electric field of

1 the order of 15-20 kV was passed through the  
2 graphite electrodes whose pointed tips were immersed  
3 in the liquid. After removal of non-dissolved black  
4 (soot) particles by filtration, vacuum evaporation  
5 of the treated liquids and washing (HPLC) with ether  
6 resulted in the isolation of red solids which were  
7 analysed by mass spectroscopy showing a presence of  
8 fullerenes in the range from  $C_{50}$  to  $C_{76}$ . The dominant  
9 fullerene molecules were  $C_{50}H_x$ , whereas contents of  
10  $C_{60}$  and  $C_{72}H_x$ ,  $C_{76}H_x$  were comparable but 3 - 8 times  
11 less than that of  $C_{50}H_x$ .

12

13 However, neither fullerenes greater than  $C_{76}$ , nor  
14 nanotubes/nanoparticles were produced this way. The  
15 process also consumes a lot of electric energy as  
16 the high-voltage arc is used. Under such arcing,  
17 tips of the electrodes are "exploded" causing  
18 graphite or metallic (if metallic electrodes are  
19 used) debris in the products.

20

21 The great disadvantage of this methodology is that  
22 the process is not self-regulated. In such a device  
23 the tips of the electrodes will be destroyed after  
24 few "explosions". One has to perform an arc through  
25 a certain gap and to check the gap during the  
26 process as the anode tip is consumed.

27

28 In observing Modak's method a safety problem arose  
29 because of the release of huge amounts of gases in  
30 the process of cracking benzene/toluene. Another  
31 problem of the Modak method is that there are no  
32 means (for example, an additional buffer gas with

1 the exception of gaseous hydrocarbons released under  
2 cracking the liquids) for regulating/controlling the  
3 cracking process to provide the desired composition  
4 of the fullerenes or to produce  
5 nanotubes/nanoparticles. As a result, HPLC is  
6 required to separate the fullerene mixture to  
7 individual species.

8  
9 The basic method for producing MWNT/buckyonions [5,  
10 9] using a DC arc discharge of 18V voltage between a  
11 6 mm diameter graphite rod (anode) and a 9 mm  
12 diameter graphite rod (cathode) which are coaxially  
13 disposed in a reaction vessel maintained in an inert  
14 (helium at pressure up to 500-700 Torr) gas  
15 atmosphere has a problem because it is not possible  
16 to continuously produce carbon nanotube/buckyonion  
17 deposits in large amounts because the deposit is  
18 accumulated on the cathode as the anode is consumed.  
19 It is required to maintain a proper distance (gap)  
20 between the electrodes.

21  
22 Oshima et al [11] suggest a complicated mechanism  
23 for maintaining the gap (preferably in the range  
24 from 0.5 to 2 mm) between the electrodes at the same  
25 DC voltage (preferably 18-21 V)/current (100-200  
26 Amp) and for scraping the cathode deposit during the  
27 process. As a result, they are able to produce up to  
28 1 gram of a carbonaceous deposit per hour per one  
29 apparatus (pair of electrodes). A  
30 nanotube/buckyonion composition of the deposit is  
31 supposed to be the same as in [5, 9], i.e.,  
32 nanotube: carbon nanoparticles (buckyonions) 2:1. A

1 specific consumption of electric energy is about 2-3  
2 kW·hour per one gram of the deposit. Complexity of  
3 the device, high specific energy consumption plus  
4 consumption of the expensive inert gas, helium, are  
5 the most important factors that restrain bulk  
6 production of MWNT/buckyonion deposits by this  
7 method.

8  
9 Instead of these methods, to produce nanotubes in  
10 bulk Olk [12] suggests simplifying a DC arc  
11 discharge device by immersing carbonaceous  
12 electrodes in a liquefied gas ( $N_2$ ,  $H_2$ , He, Ar or the  
13 like). The other arc parameters are nearly the same  
14 (18V-voltage, 80 Amps-current, 1mm-gap, 4-6 mm in  
15 diameters-electrodes). However, such a  
16 "simplification" leads to even poorer results than  
17 those in the methods mentioned above. It was  
18 possible to maintain an arc between the electrodes  
19 for just 10 seconds, and therefore the production  
20 was very low. The composition of the deposit was  
21 nearly the same as in the previous methods.

22  
23 To improve properties of the said deposits they  
24 suggest purifying and uncapping MWNTs [3,4] by using  
25 gaseous/liquid oxidants and filling the uncapped  
26 nanotubes with different materials (metals,  
27 semiconductors, etc) to produce  
28 nanowires/nanodevices. Tips of nanotubes are more  
29 reactive than side walls of buckyonions. As a result  
30 of oxidation only carbon nanotubes are finally left  
31 while buckyonions disappear.

32

1 Recently, it has been discovered that buckyonions  
2 are very promising material to produce diamonds.  
3 However, known processes produce less buckyonions  
4 than nanotubes and purifying the deposit by using  
5 known methods leads to a complete reduction of  
6 buckyonions. Therefore, it is required to find an  
7 improved process for producing or purifying  
8 buckyonions.

9  
10 It is required to uncap nanotubes to fill them with  
11 metals (to produce nanowires) or other substances,  
12 like hydrogen (to create a fuel cell).  
13 The main problem in uncapping the tubes by known  
14 methods is supposed to be that under the oxidation  
15 the tube ends become filled with  
16 carbonaceous/metallic debris that complicates  
17 filling the open-ended tubes with other materials  
18 after oxidation, finally reducing an output of the  
19 filled nanotubes.

20  
21 Chang suggests a method of encapsulating a material  
22 in a carbon nanotube [13] in-situ by using a  
23 hydrogen DC arc discharge between graphite anode  
24 filled with the material and graphite cathode. The  
25 main difference from the above mentioned methods is  
26 the use of a hydrogen atmosphere to provide  
27 conditions for encapsulating the material inside  
28 nanotubes during the arc-discharge, i.e., in-situ.  
29 All the arc discharge parameters are nearly the same  
30 as in the above mentioned processes (20V-voltage,  
31 100 Amp-current,  $150\text{\AA}/\text{cm}^2$ -current density, 0.25-2  
32 mm-gap, 100-500 Torr-pressure of the gas). The

1     presence of hydrogen is thought to serve to  
2     terminate the dangling carbon bonds of the sub-  
3     micron graphite sheets, allowing them to wrap the  
4     filling materials. Judging by TEM examination of the  
5     samples produced by this method, about 20-30% of  
6     nanotubes with diameters of approximately 10 nm are  
7     filled with copper. The range of germanium filled  
8     nanotubes is 10-50 nm and their output is much lower  
9     than that of the copper filled nanotubes. Use of a  
10    helium atmosphere (at the same pressure in the range  
11    of 100-500 Torr) instead of hydrogen leads to a  
12    preferable formation of fullerenes, copper or  
13    germanium nanoparticles and amorphous carbon (soot  
14    particles) with no nanotubes at all. A mixture of  
15    hydrogen and an inert (He) gas may be used for the  
16    encapsulation as well.

17  
18    Shi, et al [14] have reported mass production of  
19    SWNTs by a DC arc discharge method with a Y-Ni alloy  
20    composite graphite rod as anode. A cloth-like soot  
21    is produced, containing about 40% SWNTs with  
22    diameter about 1.3 nm. The most important feature of  
23    this invention is the addition of Y-Ni alloy in the  
24    anode. However, the yield of the deposits and  
25    specific energy consumption are nearly the same as  
26    in the methods described above.

27  
28    A major drawback to these prior art processes is the  
29    low quantity of non-classical fullerenes, nanotubes  
30    and buckyonions produced. Typical production rates  
31    under the best of circumstances using these  
32    processes amount to no more than 1 g/hour of a

1 carbonaceous deposit containing for 20-60% of  
2 nanotubes and 6-20% of buckyonions. Furthermore,  
3 the prior art processes are not easily scaled-up to  
4 commercially practical systems.

5  
6 In WO-A-00/61492, the applicants describe a device  
7 and method for producing higher fullerenes and  
8 nanotubes. The apparatus described in this  
9 application comprises a sealed chamber containing  
10 opposite polarity carbon (graphite) electrodes. The  
11 first electrode (electrode A) consists of a graphite  
12 pipe which is installed in vertical cylindrical  
13 openings of the cylindrical graphite matrix that  
14 forms electrode B. A free moving spherical graphite  
15 contactors is positioned above electrode A. Once an  
16 electric current is switched on, the contactor  
17 causes arcing at the electrodes. Because the  
18 contactor is free to move, the apparatus provides an  
19 auto-regulated process in which the contactor  
20 oscillates during the arcing process. The pulsed  
21 character of this oscillation provided an optimum  
22 current density and avoids saturation of the arc gap  
23 by gaseous products. This apparatus represents a  
24 significant increase in yields in comparison to the  
25 known prior art.

26  
27 It is a further object of the present invention to  
28 provide a further improvement to the apparatus and  
29 method disclosed in WO-A-00/61492.

30  
31 In the method of WO-A-00/61492, the electrodes of  
32 the arc discharge are graphite and it was believed,



1 in accordance with the understanding in the art at  
2 that time, that these electrodes acted as a carbon  
3 source for production of the fullerenes and  
4 nanotubes. Erosion of the electrodes during  
5 operation of the process was observed and this  
6 reinforced the view.

7  
8 We have now found, however, that provided the  
9 hydrocarbon liquid produces so-called "synthesis"  
10 gases (such as acetylene, ethylene, methane, or  
11 carbon monoxide) under the reaction conditions, that  
12 those gases will act as an effective carbon source  
13 and precursor for production of the nanotubes and  
14 nanoparticles.

15  
16 Thus, a new process and apparatus is required for  
17 producing carbon nanotubes and nanoparticles  
18 (especially non-classical fullerenes and  
19 buckyonions) in bulk.

20  
21 Further, single Wall Nano Tubes (SWNTs) produced by  
22 laser ablation [16] of carbonaceous targets mixed  
23 with metallic catalysts (usually, Co and Ni)  
24 typically have rope-like structures of undefined  
25 length and diameters of 1-1.4nm. For some  
26 applications it is required to cut SWNTs to shorter  
27 (100-400nm in length) pieces [17].

28  
29 SWNTs produced by an electric arc discharge between  
30 graphite electrodes containing metallic catalysts  
31 such as Ni and Y have bigger mean diameters of 1.8nm  
32 and unlimited lengths [18].

1  
2 Multi Wall Nano Tubes (MWNTs) typically have several  
3 concentrically arranged nanotubes within the one  
4 structure have been reported as having lengths up to  
5 1 mm, although typically exhibit lengths of 1  
6 micrometres to 10 micrometres and diameters of 1 -  
7 100 micrometers and diameters of 2-20nm [15]. All  
8 of the methods described in the literature to date  
9 report nanotubes of these dimensions.

10  
11 We have now discovered a methodology which produces  
12 shortened nanotubes (sh-NTs), making these nanotubes  
13 more suitable for certain applications.

14  
15 The present invention provides a process and  
16 apparatus for producing fullerenes, carbon nanotubes  
17 and nanoparticles in much larger quantities than has  
18 been possible before. The invention can be scaled up  
19 to produce commercial quantities of the fullerenes,  
20 nanotubes and nanoparticles, such as buckyonions.

21  
22 Accordingly, the present invention provides a method  
23 for producing fullerenes, nanotubes or  
24 nanoparticles, said method comprising;

- 25 a) providing a hydrocarbon liquid as an effective  
26 carbon source; and  
27 b) providing energy input, such that said  
28 hydrocarbon liquid produces acetylene,  
29 ethylene, methane or carbon monoxide.

30  
31 Preferably, the energy input can be any of the  
32 following:

1 electric arcing; resistive heating; laser; electron  
2 beam; or any suitable beam of radiation. The energy  
3 input has a key-role in triggering and controlling  
4 the element cracking of liquid hydrocarbons,  
5 providing conditions for optimal production of the  
6 "synthesis" gases (i.e. acetylene, ethylene, methane  
7 or carbon monoxide), and thus for optimal production  
8 of the nanotubes and/or nanoparticles.

9  
10 The hydrocarbon liquid may be any suitable  
11 hydrocarbon liquid and may even be a mixture of  
12 different liquids. Mention may be made of  
13 cyclohexane, benzene, toluene, xylene, acetone,  
14 paraldehyde and methanol as being suitable  
15 hydrocarbon liquids. Optionally the hydrocarbon  
16 liquid is an aromatic hydrocarbon liquid.

17  
18 Preferably, the aromatic hydrocarbon liquid contains  
19 pure aromatics and mixtures of aromatics with other  
20 liquid hydrocarbons, for instance, Co-Ni-naphtenates  
21 based on toluene solutions or toluene solutions of  
22 sulphur (which is considered to be a promoter of the  
23 growth of SWNT), etc.

24  
25 In this invention, we suggest an auto-regulated  
26 low-voltage contact electric (AC or DC) arc  
27 discharge as a good energy source.

28  
29 To produce fullerenes, it is preferable to create  
30 conditions for producing polycyclic aromatic  
31 hydrocarbon (PAHC) precursors of the fullerenes and

1 for their interactions with each other to form  
2 fullerenes (see Example 1).

3  
4 The production of fullerenes is enhanced by using  
5 selection of the geometry of the electrode system,  
6 type of the aromatic hydrocarbon, electrode  
7 material, the presence of a buffer gas.

8  
9 To produce nanotubes/nanoparticles, it is preferable  
10 to create optimal conditions for continuously  
11 producing deposits (the longer, the better) with a  
12 minimum consumption of electrical energy. More  
13 preferably an optimal voltage or type of anode can  
14 be specified for optimal production of desirable  
15 products, for example, lower or higher fullerenes,  
16 SWNTs or MWNTs or buckyonions.

17  
18 Cracking aromatic liquids provides the lowest  
19 specific energy consumption.

20  
21 By cracking aromatic-based liquids it is possible to  
22 form a very wide range of said PAHC precursors.  
23 However, under certain preferable conditions just a  
24 few PAHCs are most stable. Therefore, interacting  
25 (coagulating) with each other, they can form just a  
26 few possible combinations of carbon clusters which  
27 are annealed to a few different fullerenes. For  
28 example, in some aromatic (for instance, benzene)  
29 flames the most stable PAHC species are the  
30 following three:  $C_{16}H_{10}$ ,  $C_{24}H_{12}$  and  $C_{38}H_{14}$ . If one  
31 provides conditions for plasma-chemical interactions  
32 (coagulation) between two of these most stable

1 polycyclic precursors, only six variants of the  
2 coagulation will be possible.

3

4 These six reactions are able to produce following  
5 fullerenes:

6

7 1.  $C_{16}H_{10} + C_{16}H_{10} \rightarrow C_{28} + 2C_2 + 5H_2$

8  $\rightarrow C_{30} + C_2 + 5H_2$

9  $\rightarrow C_{32}H_2 + 4H_2$

10 2.  $C_{16}H_{10} + C_{24}H_{12} \rightarrow C_{38} + C_2 + 11H_2$

11 3.  $C_{24}H_{12} + C_{24}H_{12} \rightarrow C_{44} + 2C_2 + 12H_2$

12  $\rightarrow C_{46} + C_2 + 12H_2$

13 4.  $C_{38}H_{16} + C_{16}H_{10} \rightarrow C_{50} + 2C_2 + 13H_2$

14  $\rightarrow C_{50}(CH_2)_2 + C_2 + 11H_2$

15  $\rightarrow C_{50}(CH_2)_4 + 9H_2$

16 5.  $C_{38}H_{16} + C_{24}H_{12} \rightarrow C_{60} + C_2 + 14H_2$

17 6.  $C_{38}H_{16} + C_{38}H_{16} \rightarrow C_{74}(CH_2)_2 + 14H_2$

18  $C_{76}H_4 + 14H_2$

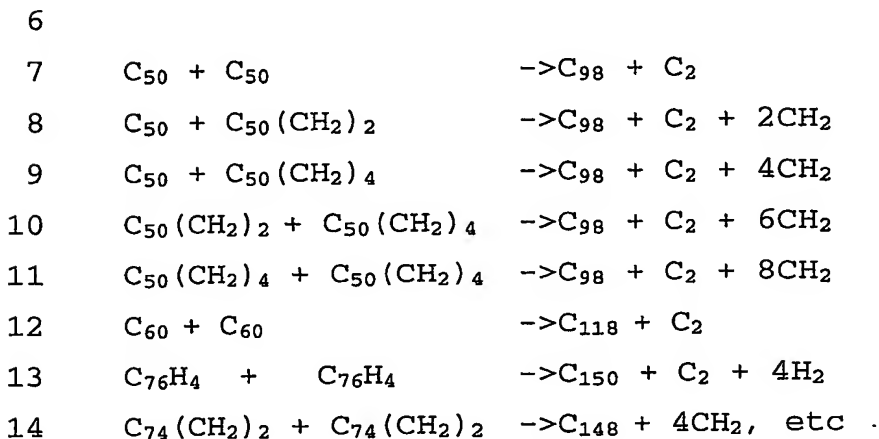
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20 One can see that if one of said precursors is  
21 reduced, it will cause a reduction or disappearance  
22 of corresponding fullerenes, for instance, for  $C_{24}H_{12}$   
23 the corresponding fullerenes are  $C_{38}$ ,  $C_{44}$ ,  $C_{46}$  and  $C_{60}$ .  
24 Therefore, if formation of  $C_{24}H_{12}$  is suppressed,  
25 production of  $C_{60}$  (and  $C_{38}$ ,  $C_{44}$ ,  $C_{46}$ ) will be  
26 suppressed as well.

27

28 Moreover, one can see that it is possible to form  
29 some fullerenes preferentially, by providing  
30 conditions for a formation of a single precursor.  
31 For instance,  $C_{74}(CH_2)_2$  or  $C_{76}H_4$  might be produced  
32 preferentially, if  $C_{38}H_{16}$  is the most abundant PAHC

1 species. Further, if proper conditions are provided  
2 to coagulate said fullerenes (or most probably their  
3 carbon cluster precursors), it will be possible to  
4 form fullerenes higher than C<sub>76</sub> using plasma-chemical  
5 interactions as following:



15

16 If C<sub>50</sub> is the most abundant fullerene species, C<sub>98</sub>  
17 will be the highest fullerene species produced.

18

19 Thus, we suggest varying the fullerene composition  
20 by adjusting conditions for preferential formation  
21 of PAHC precursors and their interaction with each  
22 other. The main features are the use and pressure of  
23 a buffer gas as well as varying the composition of  
24 the liquid and/or composition of the electrodes,  
25 varying the type and voltage of applied electric  
26 current.

27

28 Further adjustment of the cracking allows  
29 performance of a process for continuously producing  
30 nanotubes and nanoparticles.

31

1 All organic liquids are dielectrics, therefore,  
2 there is a threshold voltage for starting an  
3 electric arc discharge in the liquids and this  
4 threshold varies depending on the geometry of the  
5 electrodes.

6  
7 Thus, in the case of an electrical energy source, a  
8 range of applied voltage for optimal production has  
9 been determined. Preferably, the voltage used in  
10 nanotube production is in the range 18 to 65V. More  
11 preferably the voltage used in nanotube production  
12 is 24V to 36V. More specific energy values are  
13 preferred to form SWNTs (with smaller diameters),  
14 buckyonions and, especially, fullerenes rather than  
15 MWNTs. Therefore, applied voltages for optimal  
16 production of MWNTs should be a bit less than for  
17 buckyonions and fullerenes.

18  
19 As the arc is used as the trigger/controller, the  
20 electrodes may be constructed of any suitable  
21 material in any shape, for instance, graphite or  
22 metallic anodes in the shape of rectangular or  
23 triangular prisms, whole or truncated cylinders,  
24 flat discs, semi-spheres etc, placed inside  
25 cylindrical or square openings of the graphite,  
26 brass or stainless steel matrices.

27  
28 Preferably the electrode material should be  
29 electrically conductive and selected to withstand  
30 high temperatures in the order of 1500-4000°C.  
31 Preferably the electrode material is graphite.  
32 Graphite is a cheap solid carbonaceous material and

1 is therefore preferred for making electrodes.  
2 Refractory metals, such as tungsten and molybdenum,  
3 may be used to form electrodes. The cathode  
4 material may be selected from usual construction  
5 materials, even materials such as brass and  
6 stainless steel. These materials are particularly  
7 useful when a DC arc is being applied.

8  
9 As one of the electrodes is movable, an electrical  
10 arc between the two electrodes may be started by  
11 causing the two electrodes to touch each other,  
12 either before or after application of an electrical  
13 voltage to one of the electrodes, and then the  
14 electrodes are separated to a pre-determined gap due  
15 to gases released in the cracking process after the  
16 electrical current is flowing through the  
17 electrodes.

18  
19 The amount of voltage necessary to produce an arc  
20 will depend on the size and composition of the  
21 electrodes, the length of the arc gap, and the  
22 ambient medium (the liquid). Hydrocarbon liquids  
23 are most preferred.

24  
25 The electrical power source may provide either  
26 alternating or direct voltage to one electrode.

27  
28 A buffer gas provides for promotion of optimal  
29 condensation of carbon clusters to fullerene,  
30 nanotube and nanoparticle molecules. Generally  
31 speaking, in our process the buffer gas is mainly  
32 composed of gases released under the cracking, i.e.,



1     mainly of acetylene and hydrogen with admixtures of  
2     ethylene, methylene, ethane and methane. Thus,  
3     typically no additional buffer gas flow is required  
4     to produce said carbon allotropes. However,  
5     impressing additional buffer gases allows control of  
6     the composition of the buffer gas and its flow over  
7     the electrodes to the arc gaps and, finally, it  
8     allows control of the composition of the carbon  
9     allotrope products.

10

11     Preferably said additional buffer gas is an inert  
12     gas. More preferably said inert gas is argon.

13

14     Argon promotes arcing and processes of formation of  
15     higher fullerenes and nanotubes. When producing  
16     fullerenes, argon (as well as some oxidants, like  
17     O<sub>2</sub>, air, etc) suppresses undesirable PAHC precursors  
18     and promotes production of the desirable higher  
19     fullerenes. Thus, we found that by increasing argon  
20     flow it is possible to suppress PAHC C<sub>24</sub>H<sub>12</sub>  
21     production, one of the precursors of the fullerenes.  
22     Suppression of this precursor leads to a dramatic  
23     reduction in the production of C<sub>60</sub> and some lower  
24     fullerenes and allows the production of mainly C<sub>98</sub>.  
25     Separation of the main fullerene admixture C<sub>50</sub> is  
26     achieved by filtration through Molecular Sieves (see  
27     Example 1). Oxidants, like air or oxygen, may be  
28     useful to reduce some fullerene precursors and to  
29     modify nanotube/nanoparticle structures.

30

1 Halogens (fluorine, chlorine and bromine) may be  
2 useful for producing halogenated fullerenes and  
3 nanotubes.

4

5 However, all the additional gases except noble gases  
6 may be withdrawn as they may be produced under  
7 cracking of the aromatic liquids.

8

9 Preferably, the pressure above the liquid is pre-  
10 selected and controlled. During the cracking  
11 process, gaseous products are released and these  
12 gaseous products expand a gaseous (annealing) zone  
13 around the arc gap reducing optimal densities of  
14 carbon vapor, acetylene and other buffer gases. If  
15 the pressure above the liquid is selected to be a  
16 predetermined optimum value, the annealing (gaseous)  
17 zone will be optimised and fullerene,  
18 nanotube/nanoparticle production will be optimised.

19

20 Selecting the correct pressure above the liquid  
21 allows an increase an electric current through an  
22 arc gap without breaking the gap. However, if the  
23 pressure is too high the gap will be shorter than is  
24 required for optimal production.

25

26 Preferably an auto-regulated valve is used to  
27 release gases from the body and to maintain an  
28 optimal pressure.

29

30 Preferably the pressure above the liquid is between  
31 0.8 atm and 1.0 atm. Due to the limit of pressures  
32 at which fullerenes, nanotubes and nanoparticles can

1 be produced in sufficient quantities, the process is  
2 preferably carried out inside a hermetically sealed  
3 body or chamber. The space over the hydrocarbon  
4 liquid in the body may be evacuated by means of a  
5 vacuum pump. After the space has been evacuated, it  
6 may be partially refilled with the desired  
7 atmosphere such as a noble gas or any suitable gas  
8 mixture. More preferably, argon is used.

9  
10 The hermetically sealed body is preferably  
11 constructed of stainless steel. Opposite-polarity  
12 electrodes are placed within the body. An electrode  
13 with a smaller cross section (electrode A - anode in  
14 the DC arc) may be made as an elongated rod or pipe  
15 made of carbonaceous materials (graphite) or  
16 refractory metals, preferably of Mo or W, one ending  
17 of this rod or pipe is connected to a power supply,  
18 and a moveable graphite or metallic contactor  
19 (electrode C) suitable for starting the arcing is  
20 connected to another ending. This contactor is  
21 close to a surface of another opposite-polarity  
22 electrode with a bigger cross-section (electrode B -  
23 cathode in the DC arc).

24  
25 The current feedthrough passes through a wall of the  
26 body but is insulated from the electrical conductor  
27 so that there is no electrical contact between the  
28 electrical current source and the body. The opening  
29 in the body through which current feedthrough passes  
30 is sealed by a seal to prevent either passage of the  
31 outside atmosphere into the body or leaking of gas  
32 from the body.

1     Electrical contact between electrode A and an  
2     electrical conductor may be made by any means which  
3     will provide electrical conduction between the two.  
4     An insulator provides electrical isolation of the  
5     electrodes from the body. The insulator also  
6     provides a seal to keep the body isolated from the  
7     outside atmosphere.

8  
9     Using a free (self-movable) contactor (electrode C)  
10    allows the desired gap for the electric arc to be  
11    set at a nearly constant value since the electrodes  
12    are consumed during production of fullerenes,  
13    nanotubes and nanoparticles.

14  
15    To start the apparatus, opposite-polarity electrodes  
16    should be adjusted to barely touch. At this time,  
17    with the electrodes touching, the electrical voltage  
18    source should be activated to apply voltage to  
19    electrode A in an amount sufficient to cause an  
20    electrical current to flow from electrode A to  
21    electrode B. After the current flows, the  
22    electrodes are separated automatically because of  
23    the gases released under cracking of the liquid,  
24    cause the desired arc gap to be produced. In  
25    practice, the gap may be very small and the  
26    electrodes may appear to touch so that the arc may  
27    be described as a "contact arc".

28    When producing fullerenes, the duration of the  
29    production (0.5-8 hours) depends on solubility of a  
30    produced fullerenes in the treated liquid. In pure  
31    aromatic liquids and their mixtures most of the  
32    produced fullerenes will be dissolved into the

1 liquid. However, as soon as soot particles appear  
2 in the liquid in sufficient quantity the soot  
3 particles will adsorb nearly a half of the produced  
4 fullerenes. Therefore, using pure aromatic liquids  
5 requires extraction of the fullerenes from both  
6 fractions, the liquid and the soot.

7  
8 Increasing the operational time beyond 8 hours does  
9 not lead to a proportional increase in the fullerene  
10 output because of the destructive and synthetic  
11 processes also occurring in the process.

12  
13 Such a proportional increase of the output is only  
14 possible if the fullerenes are accumulated in the  
15 soot particles. If solubility of the fullerenes in  
16 the treated liquid is very low, the fullerenes will  
17 be forced out of solution by species having better  
18 solubility (for instant, PAHCs), so that the  
19 fullerene molecules will be continuously adsorbed by  
20 soot particles and precipitated to the bottom of the  
21 body, preventing their decomposition by the process.  
22 This allows operation of the process for an  
23 unlimited time, accumulating the fullerenes adsorbed  
24 by soot on the bottom of the body and, afterwards,  
25 isolating them from the soot using certain washing  
26 and extraction procedures. However, cracking  
27 liquids exhibiting low solubility of fullerenes  
28 (like acetone, methanol, etc) do not produce  
29 fullerenes with an output that is high enough for  
30 research and industrial applications.

1     Therefore, we suggest that the operational time when  
2     producing fullerenes should be limited to the time  
3     when the liquid becomes saturated by PAHCs.

4  
5     Afterwards, the treated liquid must be filtered  
6     using any suitable technique to separate the liquid  
7     from soot. Whatman filters or their equivalent can  
8     be used for this. As the most abundant species in  
9     the liquid and soot are PAHCs, one must  
10    remove/reduce them by any suitable washing means  
11    before isolation of the fullerenes. The liquids  
12    must be first dried in vacuum or in the atmosphere  
13    of an inert gas, like argon, N<sub>2</sub>, CO, CO<sub>2</sub>. The  
14    liquids' and soot residues are then washed with any  
15    suitable multisolvent, for instance, with methanol  
16    and/or acetone, which are characterized by the  
17    lowest solubility for fullerenes and by high  
18    solubility for PAHCs.

19  
20    Then fullerenes must be isolated from the liquid and  
21    soot by using any suitable eluent, for instant,  
22    aromatic liquids, like benzene, toluene, xylenes,  
23    chlorobenzenes, etc. The most preferable are  
24    toluene, o-xylene and chlorobenzene.

25  
26    Then one must use any suitable filtration of the  
27    eluent through a suitable nanopored material, most  
28    preferably filtering the eluent through 8/10 Å  
29    molecular sieves, to separate higher fullerenes from  
30    lower fullerenes effectively.

31

1 The lower fullerenes might then be eluted from the  
2 molecular sieves by using any suitable non-polar  
3 dissolvent, like aromatics, CS<sub>2</sub>, etc.

4

5 For producing nanotubes/nanoparticles, the process  
6 may be continued until the deposits have grown over  
7 the whole of the elongated electrodes, at which time  
8 the electrical voltage may be withdrawn  
9 automatically by using safety wires or any other  
10 suitable sensor.

11

12 Separation of carbonaceous deposits from the  
13 electrodes may be made mechanically, for instance by  
14 scraping deposits from the electrode surface.

15

16 Separation of nanotubes/nanoparticles from amorphous  
17 carbon may be made by a "soft" oxidation in air at a  
18 temperature of about 350°C for several hours (12-24  
19 hours). For bulk samples such a procedure prevents  
20 overheating of the samples because of the huge  
21 energy released by oxidation of soot particles.  
22 Then metals might be removed by careful treatment  
23 with inorganic acids (HNO<sub>3</sub>, HCl, HF, H<sub>2</sub>SO<sub>4</sub> or  
24 mixtures of such acids) at room temperature (to  
25 prevent oxidation of the spherical ends of the  
26 nanotubes and filling the opened nanotubes with  
27 metal-containing acid solution), decanting the  
28 nanotube/nanoparticle residue and washing the  
29 residue with water. Afterwards, carbon  
30 nanoparticles (onions) might be oxidized in air at  
31 535°C for several (normally, 1-4) hours.

32

1     Uncapping nanotubes might be achieved by oxidation  
2     in air at higher temperatures, normally at 600°C,  
3     for 1-2 hours.

4

5     Hydrocarbon and carbonaceous debris at the opened  
6     ends might be removed by further oxidation in air at  
7     535°C for a few minutes, coupled to heating in  
8     atmosphere of inert gas (most preferably in argon)  
9     and then in vacuum. Desirably, filling the treated  
10    nanotubes with required material (for instance, with  
11    hydrogen) should be coupled to all these  
12    abovementioned procedures, i.e. it should be done in  
13    the same cell after heating the sample in vacuum.

14

15    As stated above, our new methodology enables  
16    shortened nanotubes (sh-NTs) to be provided and  
17    these shortened nanotubes are especially suitable  
18    for certain applications.

19

20    The present invention provides shortened SWNTs (sh-  
21    SWNTs) having diameters distributed in the range 2-  
22    5nm. Preferably, the sh-SWNTs have diameters in the  
23    range 2-3nm.

24

25    Preferably, the sh-SWNTs have lengths in the range  
26    0.1 to 1 micrometers. More preferably, the  
27    shortened nanotubes have lengths in the range 0.1 to  
28    0.5 micrometers.

29

30    Consequently, the sh-SWNTs of the present invention  
31    are much shorter in length, but are of wider  
32    diameter than conventional SWNTs.



1 In accordance with a further aspect of the present  
2 invention there is provided shortened Multi-walled  
3 nanotubes (sh-MWNTs) having a mean diameter of 2 to  
4 15nm and a length of between 50 and 1000nm.

5  
6 Preferably, the sh-MWNTs have a diameter with median  
7 value of 60 to 80 Angstroms and a length of 100 to  
8 300nm.

9  
10 Preferably, the sh-MWNTs are constructed from 2 to 6  
11 layers of SWNT, usually 2 or 3 layers of SWNT.

12  
13 Thus, the sh-MWNTs according to the present  
14 invention are much shorter than those previously  
15 described in the literature.

16  
17 Powder samples of the sh-MWNTs and sh-SWNTs  
18 demonstrate relatively high electron emission at low  
19 electric fields of the order of 3-4V/micrometer.  
20 Electron emission starts at about 2V/micrometer in  
21 sh-MWNT samples.

22  
23 Unexpectedly, we have found that opening a single  
24 end of our novel nanotubes is easier to perform than  
25 in respect of existing conventional nanotubes.

26  
27 Additionally resealing the nanotubes of the present  
28 invention is simpler to perform than with  
29 conventional nanotubes.

30  
31 The hydrocarbon liquid used to produce the sh-MWNTs  
32 of the present invention may be any suitable

1 hydrocarbon. For example the liquid may be based on  
2 cyclohexane, benzene, toluene, acetone, paraldehyde,  
3 methanol, etc or may be a mixture thereof.

4  
5 In accordance with the present invention there is  
6 provided an apparatus for producing fullerenes,  
7 nanoparticles and nanotubes (in particular sh-NTs,  
8 sh-MWNTs and sh-SWNTs), the apparatus comprising a  
9 chamber capable of containing a liquid hydrocarbon  
10 reactant used to produce fullerenes, nanoparticles  
11 and nanotubes, said chamber containing at least one  
12 electrode of a first polarity and at least one  
13 electrode of a second polarity, said first and  
14 second electrodes being arranged in proximity to one  
15 another and wherein a contactor is fixedly attached  
16 to said first electrode.

17  
18 The spacing of the electrodes should be such that an  
19 electric arc can pass between them.

20  
21 Preferably, voltage applied across said first and  
22 second electrodes may be a direct voltage or an  
23 alternating voltage.

24  
25 Preferably the direct voltage is in the range 18-65  
26 Volts.

27  
28 Preferably the alternating voltage is in the range  
29 18-65 Volts rms.

30  
31 Preferably the contactor is made from graphite, but  
32 may optionally, be made from tungsten or molybdenum.

1 Preferably said contactor is spherical in shape.  
2 Optionally said contactor is hemispherical in shape.  
3 Optionally said contactor may be prismic with  
4 triangular or square cross sections, cylindrical or  
5 truncated cylindrical or flat.

6

7 Metallic contactors may also be constructed from a  
8 rectangular shape of Ti-sponge or Al cylinders

9

10 Preferably said first electrode is constructed from  
11 tungsten, but optionally the first electrode may be  
12 constructed from molybdenum or a carbon containing  
13 material such as graphite.

14

15 Preferably said first electrode is rod-shaped.

16

17 Preferably, the second electrode consists of a  
18 matrix having a plurality of cavities capable of  
19 receiving the first electrode.

20

21 Preferably, the apparatus contains a gas inlet to  
22 allow gas to be supplied to the area at or near the  
23 electrodes.

24

25 Preferably, said gas is a noble, rare or inert gas.

26

27 Preferably, said gas is argon.

28

29 Preferably, said apparatus contains cooling means  
30 which may, for example, consist of a cavity wall in  
31 the wall of the chamber through which a coolant is

1     circulated. The temperature of the coolant should  
2     be below that of the contents of the chamber.

3  
4     Preferably, said chamber contains pressure  
5     regulation means for maintaining the pressure inside  
6     the chamber at a pre-determined level.

7  
8     More preferably said desired pressure level is 0.8  
9     to 1.0 atmospheres.

10  
11    A.C. Dillon et al [17] described a method of  
12    Hydrogen Storage in carbon Single Wall Nanotubes  
13    (SWNT) with a total uptake up to 7%wt for mg-scale  
14    samples. They produce 50 wt% pure SWNTs with a  
15    yield of 150 mg/hour (about 1.5g a day for one  
16    installation) using a laser ablation method. SWNTs  
17    diameters are estimated between 1.1-1.4nm. The  
18    method involves refluxing a crude material in 3M HNO<sub>3</sub>  
19    for 16h at 120°C and then collecting the solids on a  
20    0.2micron polypropylene filter in the form of a mat  
21    and rinsing with deionised water. After drying, the  
22    carbon mat is oxidised in stagnant air at 550°C for  
23    10 min, leaving behind pure SWNTs (98wt%). Purified  
24    1-3 mg samples were sonicated in 20 ml of 4M HNO<sub>3</sub>  
25    with a high energy probe for between 10 min and 24  
26    hours at power 25 -250 W/cm to cut the SWNTs to  
27    shorter fragments. The ultra-sonic probe used is  
28    partly destroyed during the process, spoiling SWNT's  
29    with metallic particles.

30  
31    Then about 1mg of the dried sample of the cut SWNTs  
32    is annealed in a vacuum of 10<sup>-7</sup> Torr at 550°C for

1 several hours and after cooling to room temperature  
2 it is charged with hydrogen at ambient pressure.  
3 Despite such an outstanding result as 7 wt% hydrogen  
4 uptake, one can see that the method is practically  
5 useless for bulk quantities of nanotubes because of  
6 the small amounts of raw material used, huge erosion  
7 of an expensive ultra-sonic probe and difficulties  
8 of a vacuum annealing which would occur if bulk  
9 samples were used.

10

11 C. Liu et al describes a method [18] for hydrogen  
12 storage in SWNT's with bigger diameters (up to  
13 1.8nm) at room temperature and moderate pressures  
14 (about 110 atm) with a total uptake of 4.2 wt% for  
15 0.5 gram-samples. The SWNTs samples were prepared  
16 using hydrogen arc-discharge process yielding about  
17 2 g/hour of 50 - 60 wt% pure SWNTs. The SWNTs  
18 samples were then soaked in HCl acid (to open  
19 nanotubes) and then heat treated in vacuum at 500°C  
20 for two hours (to remove carbonaceous debris,  
21 hydrocarbons and hydroxyl groups at the opened  
22 ends). Hydrogen uptake was estimated on the basis  
23 of the pressure changes during storage (about 6  
24 hours). After the samples were returned to ambient  
25 pressure, some of the hydrogen (21-25 rel%) was not  
26 desorbed from nanotubes at room temperature. After  
27 applying a vacuum heating at 150°C the hydrogen was  
28 completely released from the nanotubes. In  
29 comparison to Dillon's method this method is much  
30 more productive. However, reliable vacuum heating  
31 of bulk quantities of the nanotubes is still  
32 problematic.

1     The most critical limitation for hydrogen storage in  
2     nanocarbons is the virtual impossibility of  
3     annealing hydrocarbons and carbonaceous debris at  
4     opened ends of nanopores in vacuum, especially if  
5     bulk quantities of the nanocarbons are treated on an  
6     industrial scale.

7  
8     In accordance with the present invention there is  
9     provided a method of encapsulating a gas in a  
10    nanocarbon sample, the method comprising the steps  
11    of oxidising the nanocarbon sample in order to  
12    purify the nanocarbons as much as possible and open  
13    at least one end of the nanotubes in the sample; and  
14    impressing said gas into the nanotube.

15  
16    Generally, the nanocarbon sample is oxidised at an  
17    elevated temperature, preferably not greater than  
18    550°C to oxidise metals and the metal carbides to  
19    their oxides. Most preferably the nanocarbon sample  
20    is oxidised at a temperature of between 350 and  
21    650°C, typically approximately 535°C for SWNTs or at  
22    a temperature of about 600°C to open the spherical  
23    ends of the shortened MWNTs (sh-MWNTs) nanotubes.  
24    Alternatively, the nanocarbon sample is oxidised at  
25    ambient temperature in acids to remove metallic  
26    oxides. Ideally, the nanocarbon sample is oxidised  
27    in air, typically for between 30 and 120 minutes and  
28    preferably for between about 60 and 90 minutes.

29  
30    In one preferred embodiment of the invention, the  
31    nanocarbon sample is oxidised in a three-step  
32    process comprising a first oxidation step and a

1 second oxidation step. Typically the first oxidation  
2 step is carried out at an elevated temperature,  
3 preferably not lower than 500°C, more preferably  
4 between 520 and 550°C, typically approximately 535°C  
5 for a time of between 30 and 90 minutes, ideally  
6 about 60 minutes. Typically, the second oxidation  
7 step is carried out at room temperature by soaking  
8 the nanocarbon samples in acids, preferably either  
9 in hydrochloric acid, hydrofluoric or nitric acids  
10 or mixtures thereof, for preferably between 10 to 24  
11 hours. Typically the third oxidation step is  
12 carried out at a temperature of about 600°C (for  
13 example 550 to 650°C, more preferably 580 to 620°C)  
14 for between 30 and 120 minutes, preferably between  
15 60 and 90 minutes. Ideally, the first and third  
16 oxidation steps are carried out in air.

17  
18 Preferably, the nanocarbon sample is re-heated in  
19 air prior to purging of the nanocarbon in vacuo.  
20 Typically, the re-heating step is carried out at a  
21 temperature of preferably greater than 500°C, more  
22 preferably between 520 and 650°C, typically  
23 approximately 535°C for a short time, such as for  
24 example about 3 minutes. Typically, the nanocarbon  
25 sample is purged in vacuo prior to impression of the  
26 gas into the nanocarbon. Alternatively, the re-  
27 heating step can be carried out in an atmosphere of  
28 any inert gas, most preferably in argon.

29  
30 In one embodiment of the invention, noble gases like  
31 argon, krypton, xenon or their radioactive isotopes  
32 are impressed into the nanocarbons. In such

1 instances, the gases will generally be at an initial  
2 pressure of about 70 Atm or higher (typically 70-150  
3 Atm) and will typically be impressed into the  
4 nanocarbon sample for a short period of time, such  
5 as for example about a few seconds. Alternatively,  
6 the gas may be impressed into the nanocarbon sample  
7 either in a multiple impression operation or a  
8 continuous impression operation. Thus, for example,  
9 when impressing hydrogen into a nanocarbon sample  
10 according to the invention, the hydrogen is  
11 impressed in the nanocarbon multiple times at  
12 intervals or continuously until the hydrogen  
13 pressure in the nanotube and in the donating  
14 hydrogen vessel are equalised.

15  
16 The invention also seeks to provide a method of  
17 impressing a gas such as a noble gas or hydrogen  
18 into a nanocarbon sample, which method comprises an  
19 initial step of heating the nanocarbon sample,  
20 optionally applying a vacuum to the heated sample,  
21 and impressing the gas into the sample. Generally,  
22 the heating step is carried out before the vacuum  
23 step, however, in one embodiment the heating step is  
24 carried out in an atmosphere of an inert gas,  
25 preferably in helium or argon. Typically the sample  
26 is re-heated at an elevated temperature which is  
27 preferably greater than 500°C and more preferably  
28 about 535°C, ideally for a short time such as, for  
29 example, a few minutes (up to 10 minutes).

30  
31 The invention also seeks to provide a method of  
32 preparing nanocarbon samples for gas impression,



1     which method comprises the general step of oxidising  
2     the sample according to the oxidising steps  
3     indicated above.

4  
5     Preferably, the majority of the nanotubes in the  
6     nanocarbon sample used in the method of the present  
7     invention are less than 1 micron in length, ie. they  
8     are shortened nanotubes as described above. More  
9     preferably, the majority of the nanotubes in the  
10    nanocarbon sample used in the method of the present  
11    invention are between 0.2 and 0.5 microns in length.  
12    Typically, the nanocarbon sample comprises carbon  
13    nanotubes, including their new modification, namely  
14    Single Wall Nano Horns (SWNHs) [19,20]. The SWNHs  
15    (nanohorns) are elongated Single Wall globules with  
16    conical tips of 20° and diameters of 2-3 nm and  
17    lengths of 30-50nm, thus they are very close to our  
18    SWNTs by diameters but much shorter in length. The  
19    SWNHs typically form spherical aggregates with  
20    diameters of about 80nm. In our nanocarbon samples  
21    the SWNHs' aggregates sometimes exceed 200-300 nm or  
22    even bigger. The SWNHs have an open pore structure  
23    but mostly their pores are closed (typically in  
24    three times greater). Supposedly, the SWNHs are  
25    stable during the first and second oxidation steps  
26    of the present invention and the closed pores are  
27    opened during the third oxidation step. Thus, this  
28    step must be controlled very carefully for the  
29    samples mostly containing the SWNHs as they are too  
30    short to survive in severe conditions for a long  
31    time. Thus, for such samples it is preferred to re-  
32    heat the samples in an inert gas atmosphere in order

1 to prevent further decomposition of the SWNHs during  
2 a multiple usage (a gas recharging) of the  
3 nanocarbon absorbent (for example, in a fuel cell).  
4

5 Preferably, the majority of the shortened single  
6 wall nanotubes (sh-SWNTs) in the nanocarbon sample  
7 used in the method of the present invention are  
8 between 2 and 5 nanometers in diameter.  
9

10 The nanocarbon sample may be of any size, the  
11 present invention is particularly suitable for  
12 encapsulating gases in bulk samples. That is  
13 samples having more than trace levels of  
14 nanotubes/nanohorns/nanofibers (GNFs).  
15

16 Preferably, said gas is an inert (noble) gas.  
17 Preferably, said inert (noble) gas is helium, argon,  
18 krypton, xenon and their radioactive isotopes.  
19

20 Optionally, the gas is hydrogen.  
21

22 Preferably, the method of the present invention  
23 further comprises displacing a first gas  
24 encapsulated in the nanocarbon sample with a second  
25 gas by heating the gas containing nanotubes in vacuo  
26 and impressing said second gas into the nanotube  
27 sample. Preferably, the re-heated nanocarbon sample  
28 is purged using a vacuum to remove said first gas.  
29

30 Preferably, the second gas is impressed into the  
31 nanocarbons at a pressure of approximately 70-150  
32 Atmospheres.

1 The present invention will now be described by way  
2 of example only with reference to the accompanying  
3 drawings of which:

4

5 Brief Description of Drawings

6

7 FIG. 1 is a schematic illustration of a first  
8 apparatus (Apparatus-1) for producing fullerenes,  
9 carbon nanotubes and nanoparticles according to the  
10 present invention;

11

12 FIG. 2 is a typical TOF ESI-Mass Spectrum of the  
13 eluent before filtration through Molecular Sieves of  
14 8/10Å. The Mass Spectrum was collected for 1.7 to  
15 5.9 minutes for Sample 1.

16

17 FIG. 3 shows typical TOF ESI-Mass Spectra of the  
18 eluents after filtration through Molecular Sieves of  
19 8/10Å. The Mass Spectrum was collected for 0.1 to  
20 40 minutes for Sample 2 and 0.1 to 16 minutes for  
21 Sample 3.

22

23 FIG. 4 shows TOF ESI-Mass Spectra of the eluents  
24 filtered through the Molecular Sieves of 8/10Å  
25 (Sample 3) after keeping them for three and six  
26 months;

27

28 FIGS. 5a - d are typical TEM image of deposits  
29 produced using an AC arc with applied voltage of  
30 53 Volts in Apparatus-1, (a) 3-phase current,  
31 benzene/acetone = 1:1; (b) 1-phase current, toluene;  
32 (c) "curly" nanocarbon, 3-phase current,

1 toluene/Co/Ni-naphtherates; (d) 3-phase current  
2 rectified with diodes (pulsed positive modes),  
3 benzene; and  
4

5 FIG. 6 shows an experimental dependence of the  
6 deposits compositions and their outputs versus a DC  
7 voltage applied in Apparatus-1;  
8

9 FIG. 7 is a typical TEM image of deposits produced  
10 in benzene using a DC arc with applied voltage of  
11 24 Volts using Apparatus-1;  
12

13 FIG. 8 is a typical TEM image of deposits produced  
14 in cyclohexane using a DC arc with applied voltage  
15 of 24 Volts using Apparatus-1;  
16

17 FIG. 9 is a Micro-Raman Spectrum of sh-SWNTs.  
18 Figures at the peaks indicate the diameter in nm of  
19 the sh-SWNTs.  
20

21 FIG. 10 is a typical TEM image of sh-SWNTs according  
22 to the present invention.  
23

24 FIG. 11 is a typical TEM image of sh-MWNTs according  
25 to the present invention.  
26

27 FIG. 12 shows the electron emission from a sh-MWNT  
28 powder sample. D=400 $\mu$ m, T=140 seconds, 1<sup>st</sup> scan.  
29

30 FIG. 13 is a schematic illustration of an apparatus  
31 (Apparatus-2) for producing fullerenes carbon

1     nanotubes and nanoparticles according to the present  
2     invention;

3

4     FIG. 14 shows an experimental dependence of the  
5     deposits compositions and their outputs versus a DC  
6     voltage applied in the apparatus of Fig. 13;

7

8     Fig. 15 is a schematic view of two alternative  
9     electrodes of Fig. 13;

10

11     FIG. 16 shows typical micro-Raman spectra of  
12     carbonaceous samples as produced by Rosseter Holdings  
13     and STREM;

14

15     FIG. 17 show a typical XRD profile and TEM image of  
16     deposits produced as coatings over W anodes at 30V  
17     in toluene; and

18

19     FIGS. 18a-c show typical TEM images of nanotube  
20     deposits produced over Mo anodes at 36V in toluene  
21     mixtures; and

22

23     FIG. 19 shows a TEM image of deposits produced over  
24     a Mo anode at 60V.

25

26     FIG. 20 is a scheme of a Gas Storage System  
27     realising the method of the present invention; and

28

29     FIG. 21 shows diagrams for hydrogen and argon  
30     storage in nanocarbon samples at room temperature  
31     and pressure of 70 (H<sub>2</sub>) and 110 atm (Ar).

32

1     **Example 1. Producing fullerenes.**

2

3     As shown in Fig. 1 individual cell of the apparatus  
4     for producing fullerenes includes a hermetically  
5     sealed body 1, in which a holder 2 of the electrodes  
6     A (3) and a holder 4 of the electrode B (5), and  
7     spherical graphite contactors 6 are situated above  
8     the electrodes A below a metallic grid 7. This  
9     arrangement is immersed in a hydrocarbon liquid 8  
10    and is connected to a valve 9 for flowing a buffer  
11    gas, and to a standard AC power supply 10 typically  
12    used for welding (three phase voltage, 53V, 50 Hz).  
13    Cylindrical graphite pipes 3 (electrodes A) with a  
14    smaller diameter are installed in holder 2 by using  
15    cylindrical ceramic insulators 11 and are connected  
16    to the holder using safety wires. The pipes are  
17    axially installed inside a vertical cylindrical  
18    opening of a graphite matrix 5 (electrode B).  
19    Fig.1 shows a design of the apparatus with 19 pairs  
20    of the electrodes/contactors vertically aligned in a  
21    compact hexagonal package.  
22    Graphite pipes have a length within a range of 20 to  
23    50mm or longer and external/internal diameters of  
24    4/1-2 mm provide electrode A3. Corresponding,  
25    spherical graphite contactors with a diameter within  
26    a range of 11-12.5 mm are put above the pipes onto  
27    the cylindrical openings of the graphite matrix 5  
28    (electrode B) and the openings have a diameter  
29    within a range of 13-13.5 mm. All the graphite parts  
30    were made of a Russian commercial graphite, type  
31    MPG-6.

32

1 A cylindrical stainless steel body (chamber) 20 is  
2 filled from the top by an aromatic liquid, like  
3 benzene, toluene, xylenes, etc or their mixtures to  
4 a level that is, at least, enough to cover the  
5 spherical graphite 6 contactors. Whatman filters 12  
6 are installed at the top of the body to adsorb soot  
7 particles going from the liquid with bubbles of  
8 released gases.

9  
10 Before the apparatus is switched on, air is pumped  
11 out from the body 1 through the automatic valve 13  
12 and pure argon gas is pumped through the valve 9 to  
13 the pipes to fill the empty space to a pressure that  
14 is optimal for producing a required higher  
15 fullerene. The pressure is controlled by a manometer  
16 14. Top 15 and bottom 16 lids are made of teflon to  
17 provide insulation and the possibility of observing  
18 arcing during the process. Water cooling the body  
19 (and the liquid) is flowing through the inlet 17 to  
20 the outlet 18. Rubber rings 19 seal the body.

21  
22 A buffer gas pressure in the pipe is controlled on a  
23 level that is enough to keep a gas bulb at the pipe  
24 tip, so that the gas flow through the arc will be  
25 initiated by a temperature gradient automatically as  
26 soon as the arc starts.

27  
28 As soon as the power supply 10 is switched on the  
29 process starts. With a normal AC regime an arc is  
30 generated between the contactor 6 and electrodes 3,5  
31 by turn, therefore, the both electrodes 3,5 and the  
32 contactor 6 are slowly eroded and covered with

1 cathode deposits at the same time, maintaining the  
2 electrodes geometry practically constant for hours.  
3 Using diodes allows feeding the pipes (electrode A)  
4 as anode, so just the pipes and contactors are  
5 slowly eroded in the process. This measure halves  
6 fullerene yields.

7 The arc is maintained as bright as possible, i.e. an  
8 intensity of the arc's electric current is  
9 maintained as high as possible by varying such  
10 parameters as a pressure inside the body, a liquid's  
11 composition (changing dielectric constant), arc's  
12 cross section, the type of a graphite used for the  
13 electrodes/contactors, etc. We found that at AC  
14 voltage of 53 Volts the arc's intensity of 100-  
15 300 A/cm<sup>2</sup> is enough to produce C98 with a high yield  
16 in benzene-based liquids. It corresponds to an  
17 electric current of 3-12 Amp for the arc's cross  
18 section of 3-4 mm<sup>2</sup> in the above mentioned electrode  
19 geometry.

20

21 To obtain an optimal regime for the said brightest  
22 arc, one can use an oscilloscope to control the  
23 dependence of the electric current versus time.  
24 Afterwards, an average current is roughly controlled  
25 by a proper commercial probe based on the Hall  
26 effect.

27

28 Thus, while using a bigger processor with about 100  
29 pairs of the electrodes an average current is in the  
30 range 100-110 Amps, whereas for a smaller processor  
31 with 19 pairs of the said electrodes the average  
32 current varies within the range of 15-30 Amps.



1 The duration of the producing (0.5-8 hours) depends  
2 on solubility of a produced fullerene in the treated  
3 liquid.

4  
5 If solubility of the fullerenes is higher than their  
6 concentration in the treated liquid, the fullerenes  
7 will mostly accumulate in the liquid. For instance,  
8 we have found that our apparatus produces C98 in  
9 pure benzene with a yield of about 0.4 mg per first  
10 30 min per a pair of the electrodes. The most  
11 compact geometry of the apparatus, which allows  
12 reduction of the liquid to a reasonable minimum of  
13 about 20 ml per pair of electrodes. It seems to be  
14 the concentration of C98 of 0.02 mg/ml (after first  
15 30 min), which looks much lower than the solubility  
16 for C98 in benzene. For instance, solubility of C60  
17 in benzene is about 1 mg/ml and it is the lowest  
18 among aromatic liquids. Therefore, in pure aromatic  
19 liquids and their mixtures most of the produced  
20 fullerenes will be in the liquid. However, as soon  
21 as soot particles appear in the liquid in enough  
22 quantities they will adsorb nearly half of the  
23 produced fullerenes. Therefore, using pure aromatic  
24 liquids requires extraction of the fullerenes from  
25 the both fractions, the liquid and soot.

26  
27 We have successfully produced mixtures of lower and  
28 higher fullerenes treating by 120-150 ml of pure  
29 benzene (samples 2 and 3) and/or benzene mixed with  
30 diesel fuels (samples 1) in an apparatus having one  
31 pair of the electrodes for 30 min. Sample 1 was  
32 produced without impressing a buffer gas and with an

1 air ambient above the liquid. Sample 2 was produced  
2 with impressing argon at flow inlet of about 0.002-  
3 0.003 m<sup>3</sup>/h per cm<sup>2</sup> of a total cross section of the  
4 arcs. Sample 3 was produced with impressing argon at  
5 flow inlet of about 0.001m<sup>3</sup>/h per cm<sup>2</sup> of the total  
6 arc cross section).

7

8 After the treatment all the liquids were filtered  
9 through Whatman N42 (about 0.2 g of soot was  
10 collected for samples 1 and by about 1 g of soot was  
11 collected for samples 2 and 3). The liquids and soot  
12 samples were dried in a vacuum oven at 70°C. Then  
13 dark brown residues of the benzene liquids (samples  
14 2 and 3) and black soot samples were washed for 2-24  
15 hours with hot methanol and/or acetone using  
16 magnetic stealer and/or a Soxlet extractor.  
17 After the washing the residues (of the liquids and  
18 soot samples) were extracted with 100 ml of benzene  
19 or chlorobenzene in Soxlet for 6 and 24 hours,  
20 correspondingly.

21

22 Some of samples were filtered through Molecular  
23 Sieves to separate lower fullerenes from higher  
24 fullerenes (combination of 8 Å and 10 Å granular  
25 sieves by 2-3 grams in a tube with an internal  
26 diameter of 11.2 mm). The filtered liquids were  
27 concentrated to about 2 ml and about 50µl of each  
28 sample were analysed by HPLC-MS using an analytical  
29 column and Promochem Buckyprep (preparative) column  
30 coupled with TOF ESI-Mass Spectrometer VG Bio Lab.  
31 Aldrich C<sub>60</sub>/C<sub>70</sub> fullerite and Higher Fullerene

1 reference samples were used to calibrate the HPLC-MS  
2 device.

3  
4 Fig. 2 shows HPLC (analytical column,  
5 hexane:toluene=95:5, UV signal for 330 nm), TOF ESI-  
6 Mass and UV Spectra of sample 1 that was not  
7 filtered through Molecular Sieves. TOF ESI-MS and UV  
8 spectra of Aldrich fullerite reference sample had  
9 features typical for C<sub>60</sub> and C<sub>70</sub> only. HPLC diagrams  
10 of sample 1 (Fig. 2) demonstrate a presence of  
11 numerous peaks, one of them at 3.01 min retention  
12 time corresponds to C<sub>60</sub>. MS spectra show that the  
13 analytical column regularly elutes C<sub>98</sub>, without any  
14 characteristic peaks. UV spectra collected for  
15 several registered HPLC peaks confirm this behaviour  
16 of C<sub>98</sub>. One can see, that among fullerenes higher  
17 than C<sub>60</sub>, C<sub>98</sub> is the main species (~70%) with nearly  
18 20% of C<sub>76</sub>H<sub>4</sub>-adduct and about ~10% of C<sub>60</sub>.

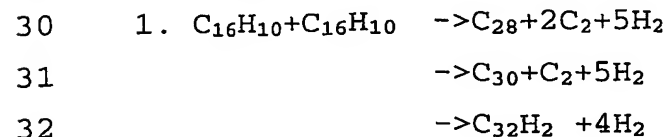
19  
20 Fig. 3 shows TOF-Mass Spectra of samples 2 and 3  
21 filtered through Molecular Sieves and kept for about  
22 3 month in glass vials. These spectra were obtained  
23 by using the HPLC-MS device equipped with the  
24 Buckuprep column. According to the spectra of sample  
25 3, C<sub>98</sub> was produced with an estimated output greater  
26 than 0.4 mg per 30 min per a pair of the electrodes  
27 (the arc's cross section is about 3-4 mm<sup>2</sup>). Thus,  
28 operating with 19-pair-electrodes apparatus allows  
29 producing greater than 7.6 mg of C<sub>98</sub> per 30 min.  
30 Traces of C<sub>150</sub> were found in sample 3.

31

1 A Mass Spectrum in Fig. 2 shows that the main  
2 fullerene species are  $C_{50}$  with adducts (we suppose  
3 that these are methylene adducts,  $C_{50}(CH_2)_2$  and  
4  $C_{50}(CH_2)_4$ ) and  $C_{98}$ , whereas  $C_{60}$  and  $C_{76}H_4$  are in 5 times  
5 lower. Species lower than  $C_{50}$  fullerene might belong  
6 to lower fullerenes ( $C_{28}$ ,  $C_{30}$ ,  $C_{32}$ ,  $C_{38}$ ,  $C_{44}$  and  $C_{46}$ ) as  
7 well as to polycyclic aromatic compounds (PAC). MS  
8 shows that the main PACs for sample 1 are  $C_{16}H_{10}$ ,  
9  $C_{24}H_{12}$  and  $C_{38}H_{14}$ , which usually are found to be the  
10 most stable hydrocarbons in aromatic flames.

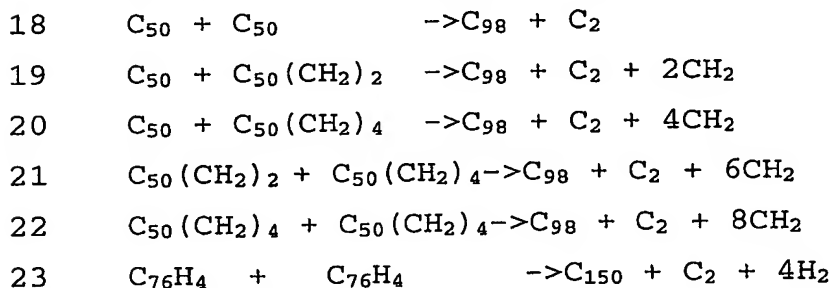
11 Fig. 3 demonstrates that most of lower species,  
12 including  $C_{50}$  fullerene and  $C_{50}(CH_2)_2$ , were separated  
13 from the samples 2 and 3 by using the filtration  
14 through Molecular Sieves with pores of 8 and 10 Å.  
15 As the Molecular Sieves are not able to separate  
16 PACs, one can conclude that the missing species are  
17 lower fullerenes and their adducts/compounds, namely  
18  $C_{28}$  (336 a.u.),  $C_{28}CH_2$  (350),  $C_{30}$  (360),  $C_{30}CH_2$  (374),  
19  $C_{32}$  (384),  $C_{32}O$  (400),  $C_{38}$  (456),  $C_{44}H_2$  (530),  $C_{46}$  (552),  
20  $C_{50}$  (600) and  $C_{50}(CH_2)_2$  (628).

21 One can discover a correlation between concentration  
22 of  $C_{16}H_{10}$ ,  $C_{24}H_{12}$  and  $C_{38}H_{14}$  (precursors) and  $C_{50}$ ,  $C_{60}$ ,  
23  $C_{76}H_4$  and  $C_{98}$  fullerenes. Relying on the correlation  
24 discovered, we suggest that all said fullerenes but  
25  $C_{98}$  are produced (under conditions of the described  
26 experiment) due to plasma-chemical interactions  
27 between two of these most stable polycyclic  
28 precursors, namely  $C_{16}H_{10}$ ,  $C_{24}H_{12}$  and  $C_{38}H_{14}$ , as  
29 following:



- 1 2.  $C_{16}H_{10} + C_{24}H_{12} \rightarrow C_{38} + C_2 + 11H_2$  ( $C_{38}$  disappeared when  
2  $C_{24}H_{12}$  was strongly reduced)
- 3 3.  $C_{24}H_{12} + C_{24}H_{12} \rightarrow C_{44} + 2C_2 + 12H_2$  ( $C_{44}$  disappeared when  
4  $C_{24}H_{12}$  was reduced)  
5  $\rightarrow C_{46} + C_2 + 12H_2$  ( $C_{46}$  disappeared when  
6  $C_{24}H_{12}$  was reduced)
- 7 4.  $C_{38}H_{16} + C_{16}H_{10} \rightarrow C_{50} + 2C_2 + 13H_2$   
8  $\rightarrow C_{50}(CH_2)_2 + C_2 + 11H_2$   
9  $\rightarrow C_{50}(CH_2)_4 + 9H_2$
- 10 5.  $C_{38}H_{16} + C_{24}H_{12} \rightarrow C_{60} + C_2 + 14H_2$  ( $C_{60}$  disappeared  
11 when  $C_{24}H_{12}$  was reduced)
- 12 6.  $C_{38}H_{16} + C_{38}H_{16} \rightarrow C_{76}H_4 + 14H_2$  (it was always  
13 present and so was  $C_{38}H_{16}$ )

15 Whereas, C<sub>98</sub> and, probably, C<sub>150</sub> are supposedly  
16 produced by plasma-chemical interactions between two  
17 of C<sub>50</sub> (or C<sub>50</sub>-adducts) and C<sub>76</sub>H<sub>4</sub> as following:



24  
25 Using different regimes (for instance, with DC of 24  
26 Volts) we found wider distributions of produced  
27 higher fullerenes, including C<sub>84</sub>, with a presence of  
28 C<sub>50</sub>, C<sub>60</sub>, C<sub>76</sub> and C<sub>98</sub> as well.

C<sub>98</sub> appears to be the most stable fullerene species among those present in sample 3. We repeated MS tests for the sample after keeping it for about 3

1 months in the testing vials. Residues were dissolved  
2 with toluene and injected in the TOF Mass  
3 Spectrometer directly. Fig. 4 shows mass spectra of  
4 the filtered eluents (samples 3) after keeping them  
5 for about three months after filtering through  
6 Molecular Sieves (FIG.4a) and then after keeping  
7 them in the testing plastic vials for an additional  
8 3 months (FIG.4b). Mass Spectra revealed mainly C<sub>98</sub>  
9 and traces of C<sub>150</sub> (Fig.4b), whereas PAC C<sub>34</sub>H<sub>16</sub> was at  
10 nearly the same level as it was before. Notice that  
11 residues of samples 3 diluted with toluene  
12 demonstrate no "chlorinated" species.

13  
14 Using our process and apparatus it is possible to  
15 produce a desirable fullerene preferentially, i.e.  
16 with few admixtures of other fullerenes and without  
17 using HPLC preparations. For instance, C<sub>98</sub> has been  
18 already produced at mg-scales. Changing regimes of  
19 the arc allows variation in the composition of the  
20 PAC precursors and, finally, varying the composition  
21 of higher fullerenes produced.

22  
23 One can understand that C<sub>50</sub> and other lower  
24 fullerene species adsorbed by the Molecular Sieves  
25 could be extracted from them by a certain elution.  
26 Thus we might have additional by-products, C<sub>50</sub>, C<sub>46</sub>,  
27 C<sub>44</sub>, C<sub>38</sub>, C<sub>32</sub>, C<sub>30</sub>, C<sub>28</sub>, etc.

28  
29  
30  
31

1     **Example 2. Producing nanotube/nanoparticle deposits**  
2     **with an AC power supply using the Apparatus of Fig.**  
3     **1.**

4  
5     Apparatus 1 can be used (Fig. 1) to produce nanotube  
6     deposits over the electrodes 3,5.

7  
8     The body is filled by an aromatic liquid 8, like  
9     benzene, toluene, xylenes, Co- and Ni-naphtenates  
10    based on toluene, etc, or their mixtures to a level  
11    that is, at least, enough to cover the contactors 6.  
12    Before the reaction commences, air is pumped out  
13    from the body through the outlet of a safety valve  
14    13 and pure argon gas is pumped through the inlet 9  
15    and through the pipes 3 (electrode A) to fill the  
16    empty space to a pressure that is optimal for  
17    producing carbon nanotubes/nanoparticles, most  
18    preferably, in the range of 600-800 Torr.

19    Afterwards, an argon flow through the opening is  
20    maintained in the range of 1-3 litre per hour per a  
21    pair of electrodes, i.e. about 20-60 litres per hour  
22    for this apparatus.

23  
24    As soon as the power supply 10 is switched on the  
25    process starts. With a normal AC regime an arc is  
26    generated between the contactor 6 and electrodes 3,5  
27    by turn, therefore, the both electrodes 3,5 and the  
28    contactor 6 are slowly eroded and covered with the  
29    deposits at the same time.

30

1 Argon flow in the pipe/opening provides the optimum  
2 conditions under which formation of  
3 nanotube/nanoparticle deposits starts.

4  
5 The production of nanotube deposits starts at first  
6 turn in the opening in which argon flow is higher.  
7 In this case, electrodes A3 are made as rods without  
8 openings. All electrodes A3 are connected to the  
9 electrode of a power supply 10 by means of a safety  
10 wire that melts when a process of formation of a  
11 nanotube/nanoparticle deposit around a certain  
12 electrode is finished.

13  
14 One can understand that the apparatus is able to  
15 produce the deposits even if electrodes A3 are  
16 placed inside the matrix's openings horizontally.  
17 All 19 electrode pairs used in this example are  
18 simultaneously fed by the power supply. The arcing  
19 between different pairs is self-arranged in line. An  
20 electric current through a certain arc gap increases  
21 while a deposit grows downward. While an edge of the  
22 deposit achieves a bottom of the opening the current  
23 increases up to 30 Amps. At this point, and the  
24 safety wire is melted and deposition stops. As soon  
25 as the process is finished in one opening the next  
26 pair of electrodes, where the argon flow is optimal,  
27 start producing a deposit.

28  
29 An AC voltage of 53V produces about 1 gram of  
30 carbonaceous deposit per 1 min per a pair of  
31 electrodes. In nearly 20 min the apparatus with 19



1 pairs of electrodes produces about 20 grams of the  
2 deposit.

3  
4 According to Transmission Electron Microscope (TEM)  
5 pictures (see Fig. 5a-c), nanotubes appear as MWNTs  
6 with diameters within the range from 2 to 20 nm,  
7 whereas buckyonions appear with sizes within the  
8 range of 4-70 nm. According to X-Ray Diffraction  
9 (XRD) profiles, these deposits mainly consist of  
10 graphitic carbon (from 40 to 90wt%) rather than  
11 MWNTs/nanoparticles (total sum is within the range  
12 1-10wt%). "Curly" nanocarbons are presented in the  
13 deposits (see at FIG. 5c).

14  
15 Using diodes allows feeding the pipes (electrodes A)  
16 as anodes, so just the pipes and contactors are  
17 slowly eroded in the process. FIG. 5d shows a  
18 typical TEM image of deposits produced with 3-phase  
19 current rectified with diodes to a pulsed positive  
20 (at electrodes A3) mode current.

21  
22 Using lower voltages looks more preferable as it  
23 allows producing the deposits with higher  
24 concentration of nanotubes.

25  
26 However, producing nanotubes and nanoparticles is  
27 more preferable with using a DC power supply.

28  
29  
30

1     **Example 3.       Producing nanotube/nanoparticle**  
2     **deposits with a DC power supply using the Apparatus**  
3     **of Fig. 1.**

4  
5     DC power supplies appear to be more preferable for  
6     producing nanotube/buckyonion deposits. FIG.6 shows  
7     an experimental dependence of the deposits  
8     compositions and their yields versus a DC voltage  
9     applied. From this dependence one can see that in  
10    this apparatus producing nanotube/nanoparticle  
11    deposits starts at voltage of about 20 V.

12   The most preferable voltage for producing MWNTs is  
13   within the range from 24 to 30V with the deposits'  
14   yields of 0.4- 1.0 g/min, correspondingly.

15   Increasing applied voltages over 36V are likely to  
16   increase yields of buckyonions, graphite and metal  
17   clusters.

18  
19   Increasing the applied voltage over 28-30 Volts  
20   requires putting one or two additional contactors  
21   above the usual one to maintain optimal arcing  
22   (these additional contactors are not eroded at all  
23   and may be used many times).

24  
25   There are two different kinds of deposits, "hard"  
26   shells and "soft" deposits, in this geometry of the  
27   apparatus.

28  
29   Surprisingly, the shells are formed around the  
30   contactors when the contactors work as anodes and,  
31   therefore, the contactors are eroded during the  
32   production. In TEM pictures deposits appear as

1 plenty of MWNTs with a rather narrow diameter  
2 distribution about  $6\text{ nm}\pm 1\text{ nm}$  with about  $6\pm 1$  layers  
3 (see Fig. 7).

4  
5 With a DC regime cathode (the matrix) is not eroded,  
6 whereas the contactors are eroded in a high extent  
7 and the anodes (pipes or rods) 3,5 are eroded  
8 slowly.

9  
10 For an applied voltage of 24V TEM, XRD and Raman  
11 spectrometry show a composition of the shells as  
12 following: MWNTs=5-30wt%, nanoparticles=5-10wt%,  
13 amorphous carbon and "curly" carbon =50wt%,  
14 graphite=50-10wt%, metals  $\leq 1-2\text{ wt}\%$ .

15  
16 The "soft" deposits are formed around the electrodes  
17 A (anodes) in case the pipes are eroded instead of  
18 the contactors. These "soft" deposits are  
19 characterized by nearly the same content of MWNTs  
20 and nanoparticles.

21  
22 Using mixtures based on cyclohexane, the apparatus  
23 produces the deposits in 3 times less but with  
24 higher contents of MWNTs and nanoparticles, than  
25 using aromatic mixtures. Fig. 8 shows a typical TEM  
26 image of deposits produced using Apparatus-1 in  
27 cyclohexane. One can see that MWNTs are mainly  
28 short, some of them are bent but practically all of  
29 them have nearly the same diameter.

30  
31 Diluting aromatics with hydrocarbon liquids, like  
32 acetone, allows increasing relative outputs of

1 MWNTs/buckyonions up to 70%wt. Using different  
2 material for electrode B (cathode) does not  
3 influence the output of the deposits. However, using  
4 a stainless steel (SS) matrix leads to the  
5 production of only "soft" deposits enriched by MWNTs  
6 and slightly depleted by SWNTs. Besides, only anodes  
7 (electrodes A) are eroded with a stainless steel  
8 matrix, i.e. arcing is situated just between the  
9 anodes (pipes/rods) and contactors.  
10 Using a brass matrix leads to a slight reduction of  
11 MWNTs/nanoparticles and an increase of "curly"  
12 nanocarbons. With a brass matrix both the anodes  
13 and contactors are eroded.

14  
15 Raman spectrometry, XRD and TEM show that  
16 impregnating electrodes A (pipes) and C (contactors)  
17 with Co and Ni oxides leads to an increase of  
18 "curly" nanocarbons, mostly composed of graphite  
19 nanofibers (GNFs), up to 40% wt., whereas total  
20 yields of the deposits are nearly the same as  
21 without Co and Ni catalysers.

22  
23 Adding soluble organometallic compounds to the  
24 liquids, like Fe-, Co- and Ni-naphtenates in toluene  
25 solutions, allows increasing yields of GNFs due to  
26 the simultaneous production of Fe, Co and Ni  
27 nanoclusters which catalyze GNFs' growth.

28  
29 Dissolving sulphur or sulphur compounds in the  
30 liquids promotes GNFs' growth further. Where using  
31 elemental sulphur dissolved in toluene up to  
32 concentration of 2-7wt% is used, a new form of GNF

1 deposit appears, very thin "cloths" or "rags" are  
2 deposited on walls of the body. We preliminary found  
3 that such deposits were mainly composed of GNFs (up  
4 to 40-50wt%), amorphous carbon (10-30wt%), carbon  
5 and metallic nanoparticles (50-20 wt%).

6  
7 Increasing the distance between the anode base  
8 (holder) and the matrix (cathode) allows growth of  
9 deposits outside the cathode matrix's openings. The  
10 deposits grow side-ward and downward (toward the  
11 anode base) over the anodes due to arcing between an  
12 edge of the deposits (cathodes) and side surface of  
13 the anodes, like the "soft" deposits grow, but cross  
14 sections of the deposits are in 2 times greater than  
15 that of deposits grown inside the openings. We found  
16 that composition of said "outside" deposits is  
17 nearly the same as composition of deposits grown  
18 inside the cathode openings and nanotubes' yields  
19 are essentially higher (in 1.3-1.6 times) than with  
20 growing inside the openings. The deposit growth  
21 continues until all the anode is covered with the  
22 deposit.

23  
24 This fact opens a lot of opportunities for  
25 continuous growth of nanotube deposits. We found,  
26 that the cathode (matrix) is required just to start  
27 the arcing (to create deposits) and afterwards the  
28 arcing goes between anodes and deposits (cathode),  
29 therefore, elongating anodes is enough for providing  
30 a continuous production of nanotube/nanoparticle  
31 deposits whereas the cathode matrix might be made as  
32 "short" as possible.

1     Elongated metallic rods or pipes might be very  
2     useful to provide such processes in Apparatus-1. We  
3     found that stainless steel rods/pipes are not very  
4     suitable anodes because of their low melting points,  
5     whereas tungsten and molybdenum anodes are good  
6     enough to replace graphite electrodes.

7  
8     We use the same apparatus (Apparatus 1) as described  
9     above with 6-7 anodes simultaneously fed by the DC  
10    power supply. The arcing between different pairs is  
11    self-arranged in line. An electric current through a  
12    certain arc gap increases while a deposit grows over  
13    the anode (electrode A) downward from the matrix's  
14    opening (soft) or around the spherical contactor  
15    (shells). When either an edge of the deposit reaches  
16    a bottom of the opening or a surface of said shells  
17    closely contacts a surface of the matrix's opening  
18    (cathode), the current increases up to 30 Amps and  
19    the safety wire is melted and production of the  
20    deposit is stopped. As soon as the process is  
21    finished in one opening the next pair of electrodes,  
22    where the argon flow is optimal, starts producing a  
23    deposit.

24  
25    Arranging feeding by 7 anodes (electrodes A)  
26    simultaneously allows constructing apparatuses as  
27    big as possible, for instant with several hundreds  
28    of said electrode pairs.

29  
30    With our apparatus of 19 anodes we produce about 10  
31    grams of the deposit per 20 min of operation,  
32    applying a DC arc voltage of about 24 Volts. TEM

1 picture (Fig. 7) shows a high quality of the deposit  
2 as produced. TEM, XRD and Raman spectrometry show a  
3 composition of the deposit as following: MWNTs=30%,  
4 nanoparticles=10%, amorphous and "curly" carbon=32%,  
5 SWNTs=25%, metals =0-3%.

6  
7 In the present invention, proper cracking of the  
8 hydrocarbon liquids driven by an optimal energy  
9 input provides the lowest specific energy  
10 consumption for producing fullerenes, nanoparticles  
11 and nanotubes.

12  
13 The invention may be embodied in other specific  
14 forms without departing from the spirit or essential  
15 characteristics thereof. The present embodiments are  
16 therefore to be considered in all respects as  
17 illustrative and not restrictive, the scope of the  
18 invention being indicated by the appended claims  
19 rather than by the foregoing description, and all  
20 the changes which come within the meaning and range  
21 of equivalency of the claims are therefore intended  
22 to be embraced therein.

23  
24 Our invention allows a continuous production of  
25 nanotube deposits with record yields of 0.2-1g/min  
26 per a pair of the electrodes with a very low  
27 specific consumption of electric energy of 50-100  
28 kW\*hour per 1 kg of the deposit produced. Using  
29 processors with several electrodes pair and  
30 elongated anodes allows to produce nanotubes and  
31 nanoparticles in bulk.

32

1     **Example 4. Producing Nanotube/Nanoparticle Deposits**  
2     **Using the Apparatus of Fig. 13**

3  
4     The apparatus for producing fullerenes illustrated  
5     in Fig. 13 includes a hermetically sealed chamber  
6     21, in which a holder 22 of the electrodes A 23 and  
7     a holder 24 of the electrode B 25, and fixed  
8     spherical or hemispherical graphite contactors 26 are  
9     situated below the electrodes A 23 above a metallic  
10    grid 27. This arrangement is immersed in a  
11    hydrocarbon liquid 28 and is connected to a valve 29  
12    (for adding a buffer gas into the chamber 1 around  
13    the electrodes), and to a standard AC power supply  
14    30 typically used for welding (three phase voltage,  
15    53V, 50 Hz).

16  
17    Cylindrical rods 23 (electrodes A) with a smaller  
18    diameter are installed in holder 22 by using  
19    cylindrical ceramic insulators 31 and are connected  
20    to the holder using safety wires. The rods 23 are  
21    axially installed inside a vertical cylindrical  
22    opening of a graphite matrix 25 (electrode B).

23  
24    Fig. 13 shows a design of the apparatus with 19  
25    pairs of the electrodes/contactors vertically  
26    aligned in a compact hexagonal package. Graphite  
27    rods have a length within a range of 20 to 50mm or  
28    longer and external/internal diameters of 4/1-2 mm  
29    provide electrode A 23. The graphite contactor is  
30    made of a Russian commercial graphite, type MPG-6.

31



1     **Example 5: Producing sh-NT and Nanoparticle Deposits**  
2     **with a DC Power Supply Using the Apparatus of Fig.**  
3     **13.**

4  
5     In use, the cylindrical stainless steel body 41 of  
6     the chamber 21 is filled from the top by a  
7     hydrocarbon liquid, like benzene, toluene, acetone,  
8     cyclohexane, paraldehyde, etc or their mixtures to a  
9     level that is, at least, enough to cover the  
10    spherical or hemispherical graphite contactors 26.  
11    Whatman filters 32 are installed at the top of the  
12    body to adsorb soot particles going from the liquid  
13    with bubbles of released gases.

14  
15    Before the apparatus is switched on, air is pumped  
16    out from the body 21 through the automatic valve 33  
17    and pure argon gas is pumped through the valve 29 to  
18    the pipes to fill the empty space to a pressure that  
19    is optimal for producing nanotubes. The pressure is  
20    controlled by a manometer 34. Top 35 and bottom 36  
21    lids are made of teflon to provide insulation and  
22    the possibility of observing arcing during the  
23    process. Water cooling the body (and the liquid) is  
24    flowing through the inlet 37 to the outlet 38.  
25    Rubber rings 39 seal the body.

26  
27    Buffer gas pressure in the pipe is controlled on a  
28    level that is enough to keep a gas bulb at the pipe  
29    tip, so that the gas flow through the arc will be  
30    initiated by a temperature gradient automatically as  
31    soon as the arc starts.  
32

1 In a preferred embodiment, Mo or W anodes (with  
2 diameters of about 3-4 mm) are hung up inside the  
3 matrix's opening from the top lid of the body.  
4 Graphite (made as spheres and/or halves of spheres,  
5 and/or prisms with triangle or square cross  
6 sections, cylinders or truncated cylinders, flat  
7 plates, etc) or metallic (for instant, made in a  
8 rectangular shape of Ti-sponge or Al cylinders)  
9 contactors 26 are attached to the free endings of  
10 the anodes closely to a surface of the matrix  
11 openings (cathode).

12  
13 Such geometry provides two opportunities for  
14 producing nanotube deposits.  
15 The first one is producing inside the openings when  
16 growth of the deposits covers over the anodes 23  
17 from below to the top of the opening (see Fig. 13).  
18 The second opportunity is growing outside the  
19 openings over the anodes 23. In this case the  
20 deposit can grow in two directions: both side-wards  
21 and upwards (see Fig. 13), thus, deposits are formed  
22 with bigger cross sections and lengths limited only  
23 by lengths of the anodes 23.

24  
25 Both opportunities are realised when free anode 23  
26 endings are placed inside the matrix's openings. If  
27 the endings are placed close to the top of the  
28 openings just a few of said inside deposit 45 will  
29 be produced (see Fig. 13). Said inside 45 and  
30 outside 47 deposits can be easily separated from  
31 each other. We found that said "inside" producing  
32 in benzene or toluene (as well as in any other

1 suitable aromatic liquid) starts at a voltage of  
2 about 18 or 19 V. The best voltage for producing sh-  
3 MWNTs is within the range 24-36 V with deposit  
4 yields of 1.2-1.8 g/min, correspondingly (see Fig.  
5 14).

6  
7 One can see that increasing voltage higher than 36V  
8 reduces sh-MWNT yields dramatically. We found just  
9 traces of sh-MWNTs with voltage of 60V, whereas the  
10 most material in TEM pictures appeared as  
11 buckyonions, soot and graphite particles and "curly"  
12 nanotubes.

13  
14 We used one anode to grow nanotube/nanoparticle  
15 deposit with the Apparatus-2 of Fig. 13. Inside 45  
16 and outside 47 deposits were produced in  
17 toluene/acetone mixture using one W anode (of 3 mm  
18 in diameter). A half of a graphite spherical  
19 contactor (diameter of about 12 mm) impregnated with  
20 Co and Ni oxides (by 3%wt. by the metals) was  
21 attached to a free ending of the anode rod and  
22 placed in a top of a graphite matrix's opening  
23 (cathode) to start arcing at an applied DC voltage  
24 of 30 Volts. At the beginning of the arcing an  
25 electric current was about 40 to 60 Amps (producing  
26 an "inside" deposit with a yield of about 0.7g/min)  
27 then it was in the range from 20-50 Amps producing  
28 an "outside" deposit (with nearly the same yield of  
29 0.5 g/min). Both deposits were easily detached from  
30 the electrodes and from each other. After the  
31 process the W rod was slightly eroded at the free  
32 end. The inside 45 and outside 47 deposits (as

1 produced) contains sh-MWNTs= 20 - 40wt%, polyhedral  
2 particle, graphite "curly" and amorphous nanocarbons  
3 and metals (0.5 - 5wt%). Fig. 15 shows XRD profiles  
4 of said "inside" deposit and MWNT-deposit as  
5 produced by STREM (shells).

6  
7 An outside deposit 47 of 30 grams per 12 min (with a  
8 yield of 2.5 g/min) was produced with Mo anode (2  
9 rods with diameters of 2.5 mm and lengths of about  
10 10 cm) submerged in a mixture of toluene with Co-  
11 and Ni-naphtenates (on a basis of toluene). Co and  
12 Ni elemental concentration in said mixture was by  
13 about 3%wt. A half of a graphite spherical contactor  
14 (diameter of about 12 mm) impregnated with Co and Ni  
15 oxides (by 3%wt. by the metals) was attached to free  
16 endings of the rods and placed in a top of a  
17 graphite matrix's opening (cathode) to start arcing  
18 at an applied DC voltage of 36 Volts. At the  
19 beginning of the arcing an electric current was in  
20 the range 20-30 Amps (producing a small "inside"  
21 deposit) then it was varied in the range from 6 to  
22 60 Amps (mean current about of 25 Amps) producing a  
23 huge outside deposit 47. Both Mo rods were  
24 completely eroded and/or melted during the arcing  
25 between the rods and the deposit.

26  
27 Fig. 16 shows Raman spectra of the deposit and of  
28 SWNT (STREM) sample, both as produced.

29 One can see that all features, Raman peaks  
30 corresponding to certain arm-chair SWNTs, are the  
31 same in both spectra but our deposit contains SWNTs  
32 of bigger diameters, mainly of 2.2 and 2.7 nm that

1 corresponds to armchair SWNTs (16,16) and (20,20),  
2 correspondingly, whereas STREM-SWNT mostly consists  
3 of (11,11), (10,10) and (9,9) armchair SWNTs with  
4 few of (16,16) and (20,20) and higher.

5  
6 TEM pictures (see Fig. 18a-c) of the deposit confirm  
7 these findings. Fig. 18a shows sh-MWNTs and "curly"  
8 nanocarbons over all the area shown. A more  
9 detailed look at the SWNTs' clusters reveals sh-  
10 SWNTs' lengths and diameters within the range 0.1-  
11 1  $\mu\text{m}$  and 2-5 nm, correspondingly.

12  
13 A High-Resolution TEM picture (Fig. 18b) shows that  
14 sh-MWNTs have one semispherical and one conical end.  
15 Oxidising in air at temperatures up to 600°C for 1-  
16 1.5 hours allows opening all spherical ends of MWNTs  
17 independently from number of the MWNTs' layers and  
18 leaving the conical ends to be intact (see Fig.  
19 18c).

20  
21 We also found that producing deposits over graphite  
22 contactors, containing mainly nanoparticles and  
23 "curly" nanocarbons was possible with the apparatus  
24 of the present invention at applied voltages of 60V  
25 or a bit higher. Fig. 8 shows a typical TEM image  
26 of deposits produced over Mo anodes at 60V in  
27 toluene.

#### 28 29 **Example 6. Production of Shortened Nanotubes**

30  
31 To produce the sh-MWNTs and sh-SWNTs as described  
32 above, the apparatus of Fig. 13 (Apparatus-2) and

1 the method of described in Examples 4 and 5 was  
2 employed using a tungsten 3mm diameter rod and  
3 cyclohexane/acetone/toluene (for sh-MWNTs) and  
4 toluene/Co/Ni-naphtenates (for sh-SWNTs) mixtures  
5 as the hydrocarbon liquids. A DC voltage of 24Volts  
6 (3 pairs of normal car batteries connected in  
7 parallel) was applied to provide an arc current of  
8 20-40Amps. A narrow sh-MWNT deposit (of about 80g)  
9 was grown over a 40 cm-length W rod for about 4  
10 hours. TEM tests shown, that said deposit contained  
11 about 20-40%wt. the sh-MWNTs. A 15 gram-deposit  
12 produced with Co/Ni-catalysts for about 10 min  
13 mostly contained "curly" nanocarbon forms including  
14 shorten GNFS (lengths were less than 1 micron), the  
15 sh-MWNTs (1-5%) and the sh-SWNTs (of about 1%).

16

#### 17 **Example 7. Gas Storage**

18

19 A nanocarbon deposit of 30 grams was produced using  
20 the method of Example 5 in 12 min (with a yield of  
21 2.5 g/min) with using a Molybdenum (Mo) (2 rods with  
22 diameters of 2.5 mm and lengths of about 10 cm)  
23 submerged in a mixture of toluene with Co- and Ni-  
24 naphtenates (on a basis of toluene). Co and Ni  
25 elemental concentration in said mixture was by about  
26 3%wt. A half of graphite spherical contactor  
27 (diameter of about 12 mm) impregnated with Co and Ni  
28 oxides (by 3% wt by the metals) was attached to free  
29 endings of the rods and placed in a top of a  
30 graphite matrix's opening (cathode) to start arcing  
31 at an applied DC voltage of 36 volts.

32

1     TEM, XRD and micro-Raman spectrometry show the  
2     composition of the deposit (as produced) to be as  
3     follows: sh-MWNTs (shortened multiple wall  
4     nanotubes) about 30wt%, total "curly" nanocarbons  
5     about 50wt%, the remainder are carbon and metallic  
6     nanoparticles.

7  
8     Figs. 18a - 18c represent TEM images of the deposit  
9     which are composed mainly of a "curly" material  
10    (supposedly sh-GNFs, sh-SWNTs and SWNHs) and sh-  
11    MWNTs. Lengths of shortened nanocarbons in the  
12    deposits are not in excess of 1 micron, and are  
13    typically within the range 0.2-0.5 microns.

14  
15    Therefore, there is no need to cut nanotubes into  
16    shorter fragments. It is only required to purify  
17    and open them only.

18  
19    Fig. 16 shows Raman spectra of the deposit and of  
20    SWNT (STREM company) sample, both as produced. One  
21    can see that all features, Raman peaks corresponding  
22    to certain arm-chair SWNTs are the same in both  
23    spectra but our deposit contains SWNTs of bigger  
24    diameters, mainly of 2.2 and 2.7 nm that corresponds  
25    to armchair SWNTs and (20, 20) correspondingly,  
26    whereas STREM-SWNT mostly consists of (11,11)  
27    (10,10) and (9,9) armchair SWNTs with few of (16,16)  
28    and (20,20) and higher. Thus, in average our SWNTs  
29    are slightly bigger in diameter than those of Liu et  
30    al (up to 1.8 nm) [18].

31

1 The deposit was treated at room temperature with  
2 mixtures of nitric and fluoric acids for 16-21 hours  
3 (to remove metals without any oxidation of  
4 nanotubes), then cleaned with distilled water, dried  
5 and oxidised in air at 535°C for 1 hour. After  
6 treatment the deposit was reduced to 25 grams (83%  
7 of initial weight) and its composition revealed from  
8 XRD and Raman data was as following: shortened  
9 Multi-Wall Nanotubes (sh-MWNTs) about 35 wt %, and  
10 total of sh-GNFs, sh-SWNTs and SWNHs about 55-60  
11 wt %. This shows that producing nanotubes with a  
12 total of 90-95% (or even higher) and a yield of 2  
13 g/min is possible using our method. The percentages  
14 of sh-GNFs, sh-SWNTs and SWNHs in our samples were  
15 very close to those of Liu et al for SWNTs (50-  
16 60wt%) [18].

17

18 High Resolution TEM picture (Fig. 18b) shows that  
19 both, spherical and conical ends of MWNTs (including  
20 one Triple Wall Nano Tube) stayed intact after such  
21 oxidative treatment, whereas further oxidation in  
22 air at temperatures up to 600°C for 1-1.5 hours  
23 opened all of the spherical ends of the MWNTs  
24 independently from number of the MWNTs layers and  
25 left the conical ends intact (see Fig. 18c). This  
26 is highly significant for the survival of very short  
27 SWNHs having conical tips and for opening SWNTs  
28 which have spherical caps.

29

30 About 10 grams of such a sample was re-heated in air  
31 at 535°C for about 3 minutes and then this hot  
32 sample was immediately put in a cylindrical



1 stainless steel cell (of about 12 ml capacity) that  
2 was immediately connected to a storage system (see  
3 Fig. 21) and vacuum pump 2 was switched on to purge  
4 the sample.

5  
6 A vacuum (oil-free) pump was withdrawn after pumping  
7 for about 10-15 minutes and then Argon was shortly  
8 (1-2 sec) impressed into the cell through a Gas line  
9 53 from a Gas Container 54 at initial pressure of  
10 about 110 atm that was controlled with a normal  
11 Pressure Manometer 55. A stainless steel "cotton"  
12 filter 56 was used to prevent losses of the samples.  
13 A total capacity of the storage system was estimated  
14 to be about 20 ml (without a nanotube sample). By  
15 immersing samples in acetone, we estimated that  
16 "solid" part of 10 grams of the nanotube samples  
17 took about 5ml i.e. a total capacity of a gas system  
18 (including inside nanotubes cavities) was about 15  
19 ml. This figure allowed estimating a Gas uptake on  
20 a basis of pressure changes. The Gas Storage System  
21 was leak-free.

22  
23 Fig. 22 shows Argon storage for the first 30 min.  
24 One can see that Argon storage of about 7.6 wt% was  
25 achieved even without annealing of the sample.

26  
27 We stored Hydrogen gas in the same sample after re-  
28 heating it in a vacuum oven at 150°C for 2 hours.  
29 An initial pressure of H<sub>2</sub> was about 70 atm. As the  
30 initial pressure was lower, we impressed Hydrogen 8  
31 times repeatedly in each 20 minutes (as soon as the  
32 pressure in the gas system dropped for 25-13 atm and

1 Hydrogen storage was practically stopped). This  
2 allowed us "pumping" the nanocarbon sample with  
3 hydrogen up to 2 wt% after 8 cycles (160 min)  
4 without annealing the sample (see Fig. 22). One can  
5 see that this result was very close to the result by  
6 Liu [18] for a run without a vacuum annealing.  
7 Weighing the sample after withdrawal of the pressure  
8 shown that about 40 mg (0.4 wt% ie about 1/5 of a  
9 total hydrogen stored) of hydrogen was left in the  
10 sample.

11  
12 Another 10 grams-sample was put in the cell and re-  
13 heated in ambient (air) atmosphere at 500°C-535°C for  
14 about 3 minutes using a heater 57 with thermo-  
15 controlling device 58. Then a vacuum was created  
16 and maintained in the cell and while the heater was  
17 withdrawn letting the sample cool to room  
18 temperature. Afterwards, hydrogen was repeatedly (8  
19 times in each 20 minutes) impressed in the cell at  
20 70 atm. After 160 min (8 cycles) Hydrogen uptake of  
21 3.9 wt% was achieved (see Fig. 22) that was even  
22 slightly higher than Liu's hydrogen uptake after the  
23 same time (for a run with vacuum annealing). Weight  
24 the sample after a withdrawal of the pressure shown  
25 that about 90 mg (0.9 wt% ie. about 23 rel % of a  
26 total hydrogen stored of hydrogen was left in the  
27 sample. This hydrogen was released under re-heating  
28 the sample in a vacuum oven at 150°C for about 2  
29 hours.

30

31 Thus, at an initial pressure of 70 atm about 4wt%  
32 might be stored in 10 grams of about 50-60wt% of sh-

1      GNFs, sh-SWNTs and SWNHs with a destiny of 37.5 kg  
2      H<sub>2</sub>/m<sup>3</sup>.  
3  
4      Improvements and modifications may be incorporated  
5      herein without deviating from the scope of the  
6      invention.

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1     **Claims**

2

3     1.   A method for producing fullerenes, nanotubes or  
4         nanoparticles, said method comprising:

5         a)    providing a hydrocarbon liquid as an  
6               effective carbon source; and

7         b)    providing energy input, such that said  
8               hydrocarbon liquid produces acetylene,  
9               ethylene, methane or carbon monoxide.

10

11     2.   The method as claimed in Claim 1 wherein said  
12         hydrocarbon liquid comprises an aromatic  
13         hydrocarbon liquid.

14

15     3.   The method as claimed in Claim 2 wherein said  
16         hydrocarbon liquid comprises benzene, toluene,  
17         xylene.

18

19     4.   The method as claimed in any one of Claims 1 to  
20         3 wherein the energy input is electricity,  
21         resistive heating, a laser or electron beam.

22

23     5.   The method as claimed in Claim 4 wherein the  
24         energy input is electricity and is provided at a  
25         voltage of 18 to 65V.

26

27     6.   The method as claimed in Claim 5 wherein the  
28         electricity is provided at a voltage of 24 to  
29         36V.

30

- 1       7.   The method as claimed in any of Claims 4 to 6  
2       wherein an electric arc across two electrodes is  
3       created as the energy input.  
4
- 5       8.   The method as claimed in Claim 7 wherein the  
6       electrodes are formed of graphite, tungsten or  
7       molybdenum.  
8
- 9       9.   The method as claimed in any preceding Claim  
10      wherein a buffer gas is also provided.  
11
- 12      10.  The method as claimed in Claim 9 wherein said  
13      buffer gas is argon.  
14
- 15      11.  The method as claimed in either one of Claims 9  
16      and 10 wherein the buffer gas is present at a  
17      pressure of between 0.8 and 1.0 atmospheres.  
18
- 19      12.  The method as claimed in any preceding Claim  
20      wherein after step b) nanotubes and  
21      nanoparticles are separated by mechanical  
22      removal of carbonaceous deposits on the  
23      electrodes, followed by oxidation, treatment  
24      with acids and decanting the  
25      nanoparticle/nanotube residue.  
26
- 27      13.  The method as claimed in any one of Claims 1 to  
28      11 wherein after step b) fullerenes are  
29      separated from the hydrocarbon liquid and soot  
30      by using an eluent followed by filtration  
31      through an 8-10Å sieve.  
32



- 1     14. Shortened single walled nanotubes (sh-SWNTs)  
2         having a diameter of from 2 to 5 nm.  
3
- 4     15. Shortened SWNTs according to Claim 14 having a  
5         length of from 0.1 to 1  $\mu\text{m}$ .  
6
- 7     16. Shortened SWNTs according to Claim 15 having a  
8         length of from 0.1 to 0.5  $\mu\text{m}$ .  
9
- 10    17. Shortened SWNTs according to any of Claims 14 to  
11         16 having a diameter of from 2 to 3 nm.  
12
- 13    18. Shortened multi-walled nanotubes (sh-MWNTs)  
14         having a mean diameter of from 2 to 15 nm and a  
15         length of between 50 to 1000 nm.  
16
- 17    19. Shortened MWNTs as claimed in Claim 18 having a  
18         median diameter of 60 to 80Å and a length of 100  
19         to 300 nm.  
20
- 21    20. Shortened MWNTs as claimed in either one of  
22         Claims 18 and 19 constructed from 2 to 6 layers  
23         of SWNTs.  
24
- 25    21. An apparatus for producing fullerenes, nanotubes  
26         or nanoparticles, the apparatus comprising a  
27         chamber capable of containing a liquid  
28         hydrocarbon reactant used to produce fullerenes,  
29         nanoparticles and nanotubes, said chamber  
30         containing at least one first electrode having a  
31         first polarity and at least one second electrode  
32         having a second polarity, said first and second

1 electrodes being arranged in proximity to one  
2 another and wherein a contactor is fixedly  
3 attached to said first electrode.  
4

5 22. The apparatus as claimed in Claim 21 wherein  
6 said contactor is made from tungsten, molybdenum  
7 or graphite.  
8

9 23. The apparatus as claimed in either one of Claims  
10 21 and 22 wherein said contactor is spherical.  
11

12 24. The apparatus as claimed in any one of Claims 21  
13 to 23 wherein said first electrode is made from  
14 tungsten, molybdenum or graphite.  
15

16 25. The apparatus as claimed in any one of Claims 21  
17 to 24 wherein said first electrode is rod-  
18 shaped.  
19

20 26. The apparatus as claimed in any one of Claims 21  
21 to 25 wherein said second electrode consists of  
22 a matrix having a plurality of cavities capable  
23 of receiving a first electrode.  
24

25 27. The apparatus as claimed in any one of Claims 21  
26 to 26 wherein said apparatus contains a gas  
27 inlet to allow gas to be supplied to an area at  
28 or near the electrodes.  
29

30 28. The apparatus as claimed in any one of Claims 21  
31 to 27 wherein said apparatus includes cooling  
32 means.

1

2 29. The apparatus as claimed in Claim 28 wherein  
3 said cooling means consists of a cavity wall in  
4 the wall of the chamber through which a coolant  
5 is circulated.

6

7 30. The apparatus as claimed in any one of Claims 21  
8 to 29 wherein said chamber includes pressure  
9 regulation means for maintaining the pressure  
10 inside the chamber at a pre-determined level.

11

12 31. A method of encapsulating a gas within a  
13 nanocarbon sample, said method comprising the  
14 following steps:

- 15 a) oxidising the nanocarbon sample  
16 sufficiently to open one end of at least  
17 some of the nanotubes in the sample;  
18 b) impressing said gas into the opened  
19 nanotubes.

20

21 32. The method as claimed in Claim 31 wherein the  
22 nanocarbon sample is oxidised at ambient  
23 temperature in acid for 30 to 120 minutes.

24

25 33. The method as claimed in Claim 31 wherein the  
26 nanocarbon sample is oxidised at a temperature  
27 of from 350 and 650°C.

28

29 34. The method as claimed in any one of Claims 31 to  
30 33 wherein the nanocarbon sample is oxidised by:  
31 i) heating to a temperature of above 500°C  
32 for 30 to 90 minutes;

- 1           ii) soaking the nanocarbon sample of step i)  
2           in hydrochloric, hydrofluoric or nitric  
3           acids for 10 to 24 hours; and  
4           iii) heating the nanocarbon sample of step ii)  
5           to a temperature of about 600°C for 30 to  
6           120 minutes.

7

8       35. The method as claimed in any one of Claims 31 to  
9       34 wherein said gas is impressed into said  
10       opened nanotubes by heating said nanocarbon to a  
11       temperature of 520°C to 650°C for up to 10  
12       minutes in an atmosphere of the gas.

13

14       36. The method as claimed in any one of Claims 31 to  
15       34 wherein said gas is impressed into said  
16       opened nanotubes by heating said nanocarbon  
17       sample to a temperature of 520°C to 650°C for up  
18       to 10 minutes, purging said heated sample in  
19       vacuo and then exposing said sample to said gas  
20       at a pressure of 70 atmospheres or higher.

21

22       37. The method as claimed in any one of Claims 31 to  
23       36 wherein said nanocarbon sample contains  
24       shortened nanotubes having a diameter of 1  $\mu\text{m}$  or  
25       less.

26

27       38. The method as claimed in any one of Claims 31 to  
28       37 wherein said gas is hydrogen, helium, argon,  
29       krypton, xenon or radioactive isotopes thereof.

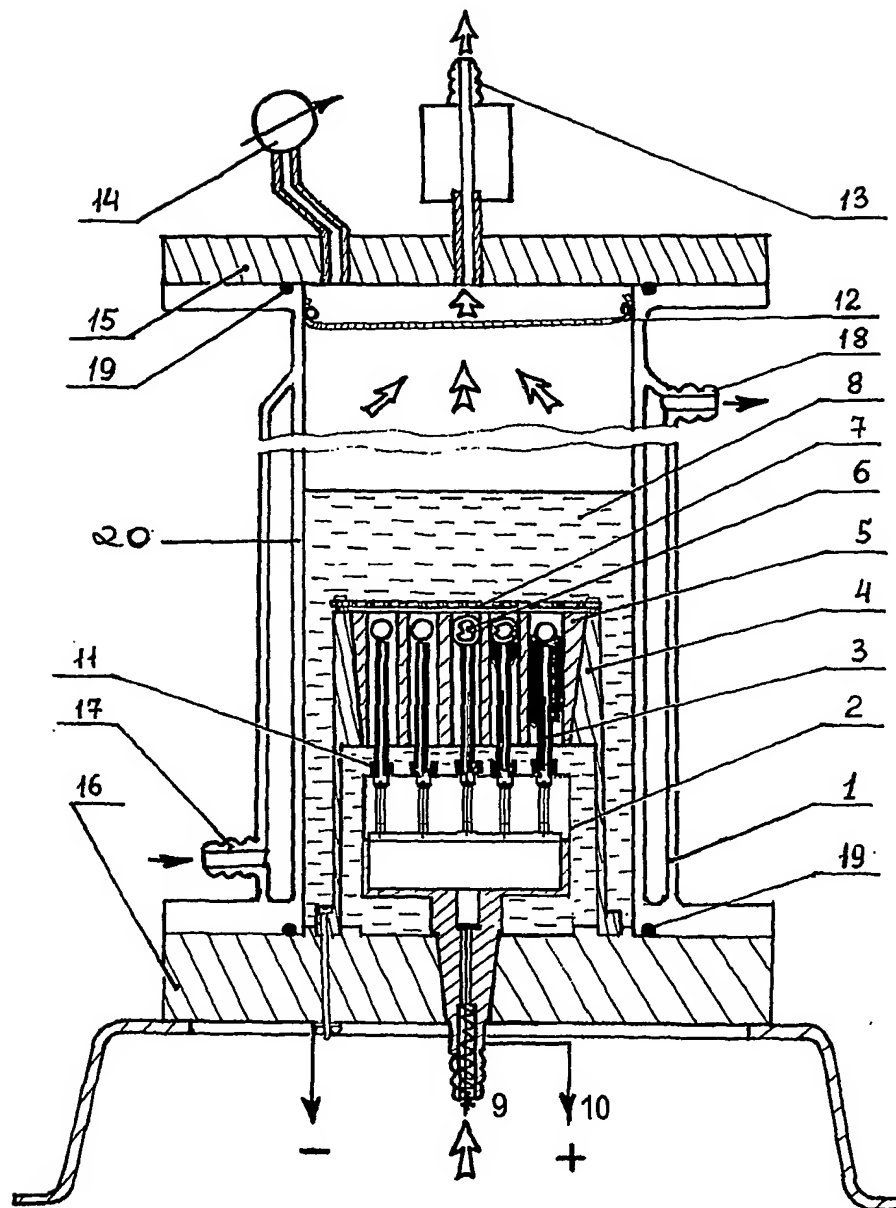
30

31       39. A method of displacing a first gas encapsulated  
32       in a nanocarbon sample and replacing said first

1           gas with a second gas, said method comprising  
2           heating the nanocarbon sample *in vacuo* and  
3           impressing said gas into said sample.

4

5       40. The method as claimed in Claim 39 wherein said  
6           second gas is impressed into the nanocarbon  
7           sample at a pressure of approximately 70 to 150  
8           atmospheres.

*Fig. 1*

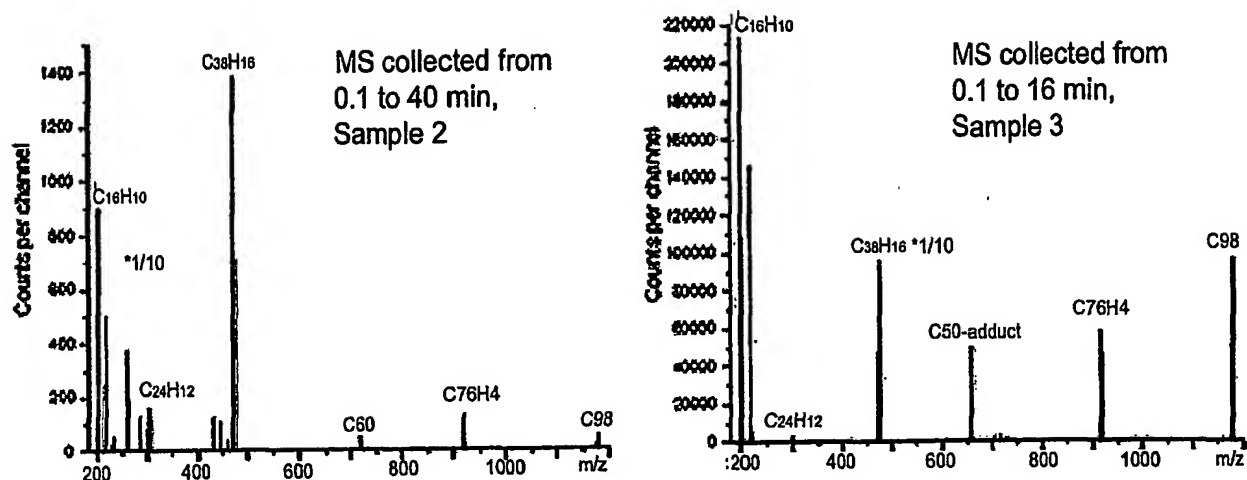


Fig. 3

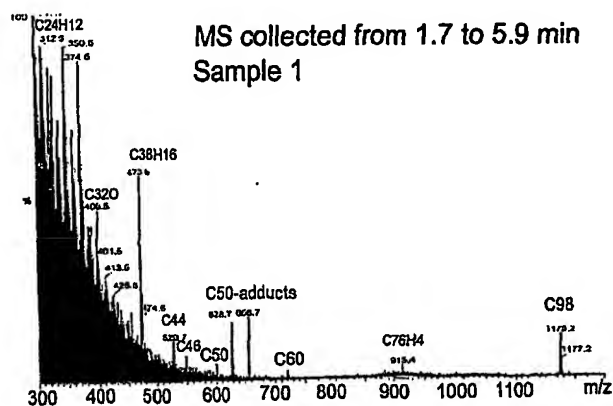


Fig. 2

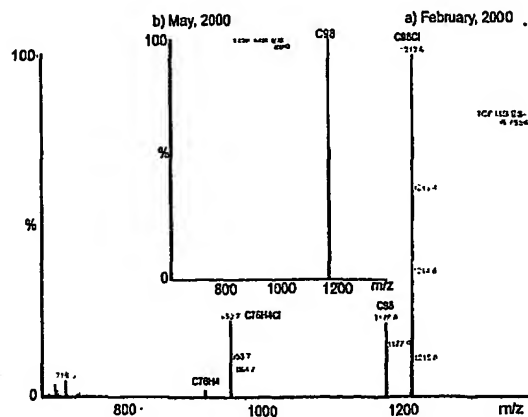


Fig. 4

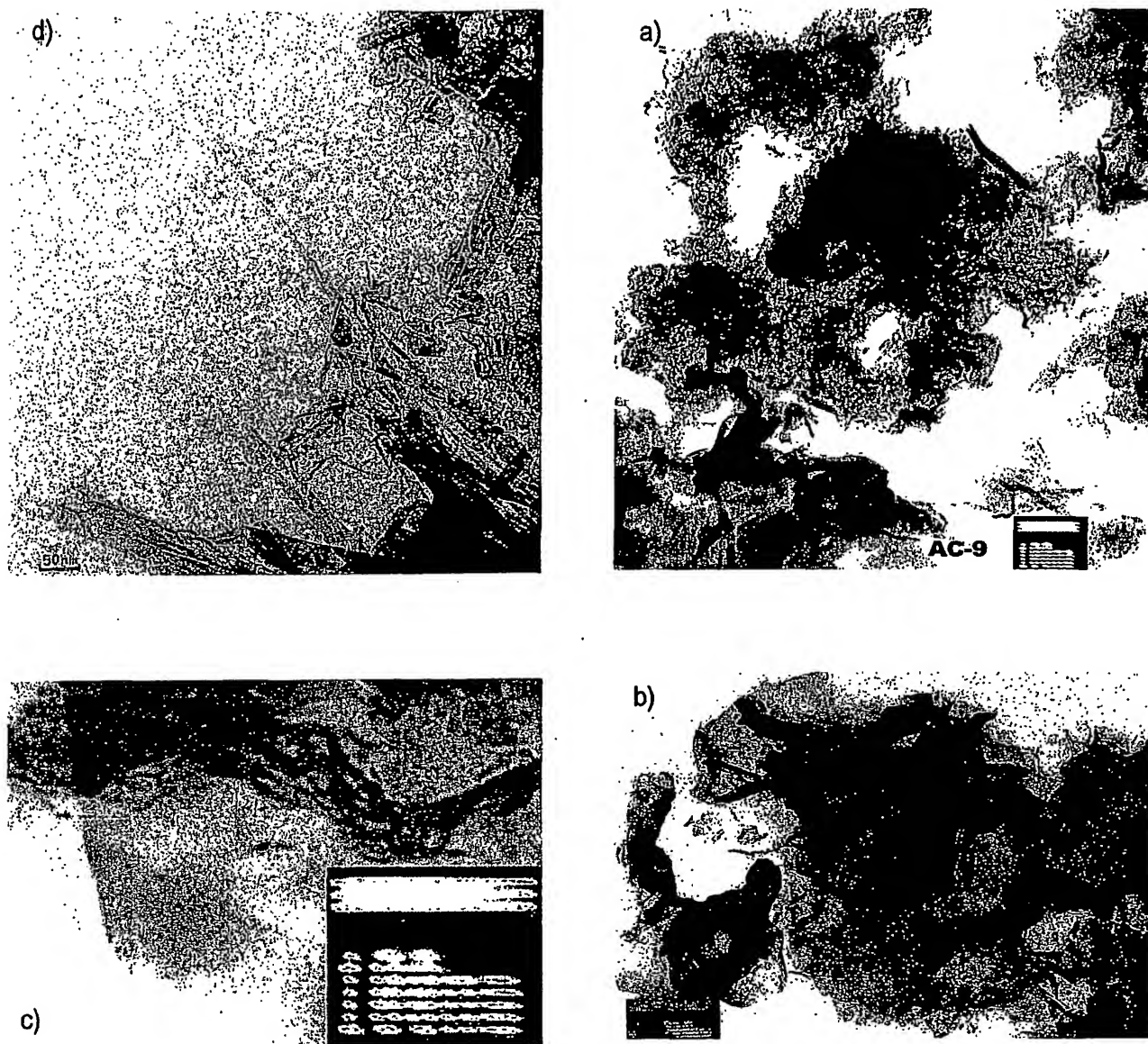


FIG.5 TEM images of deposits produced using AC (53Volts) arc in Apparatus-1:  
a - 3-phase current, benzene/acetone=1:1; b - 1-phase current, toluene  
c - bundle of tangled SWNTs, 3-phase current, toluene/Co/Ni-naphtenates  
d - 3-phase current rectified with diodes (pulsed positive modes), benzene





FIG.8 TEM image of deposits produced with Apparatus-1 (DC) in cyclohexane



FIG.7 TEM image of deposits produced with Apparatus-1 (DC) in benzene

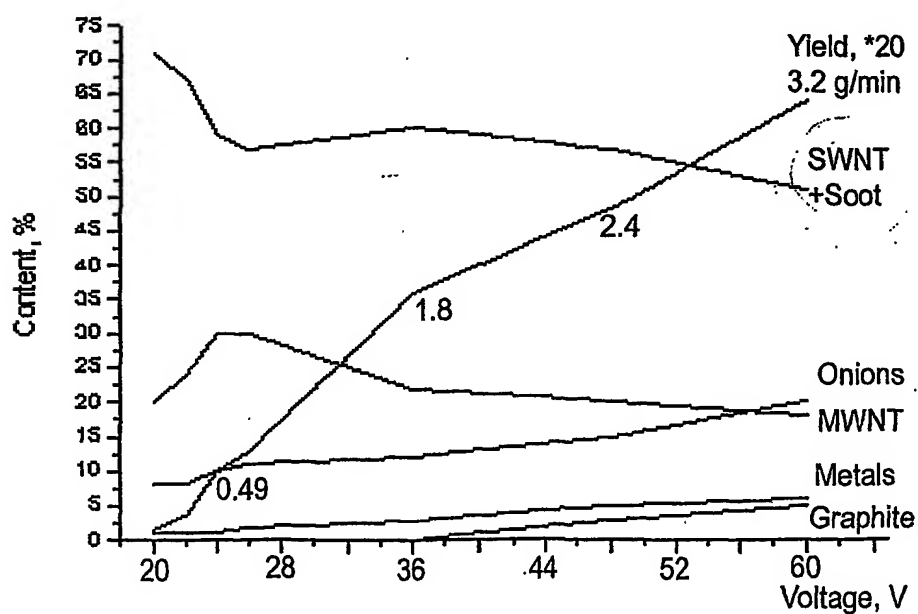


FIG.6 Composition and Yield of deposits vs DC voltage in Apparatus-1

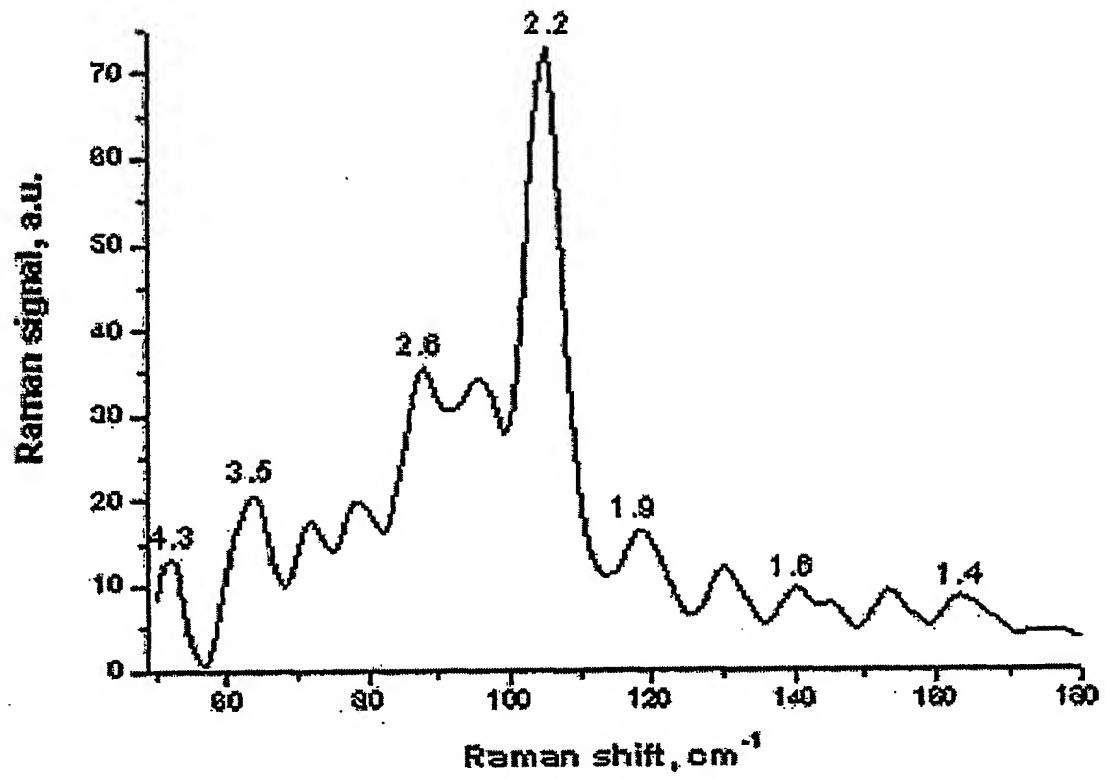


FIG. 9

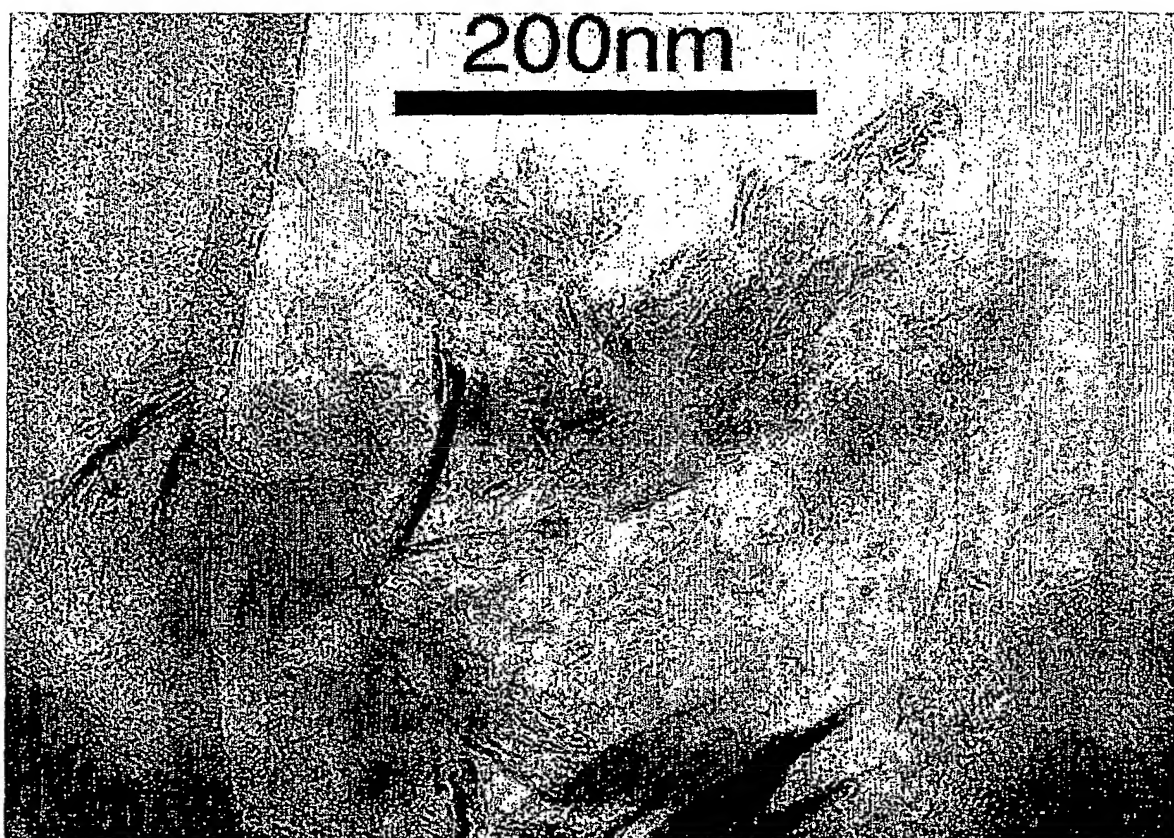


FIG. 10

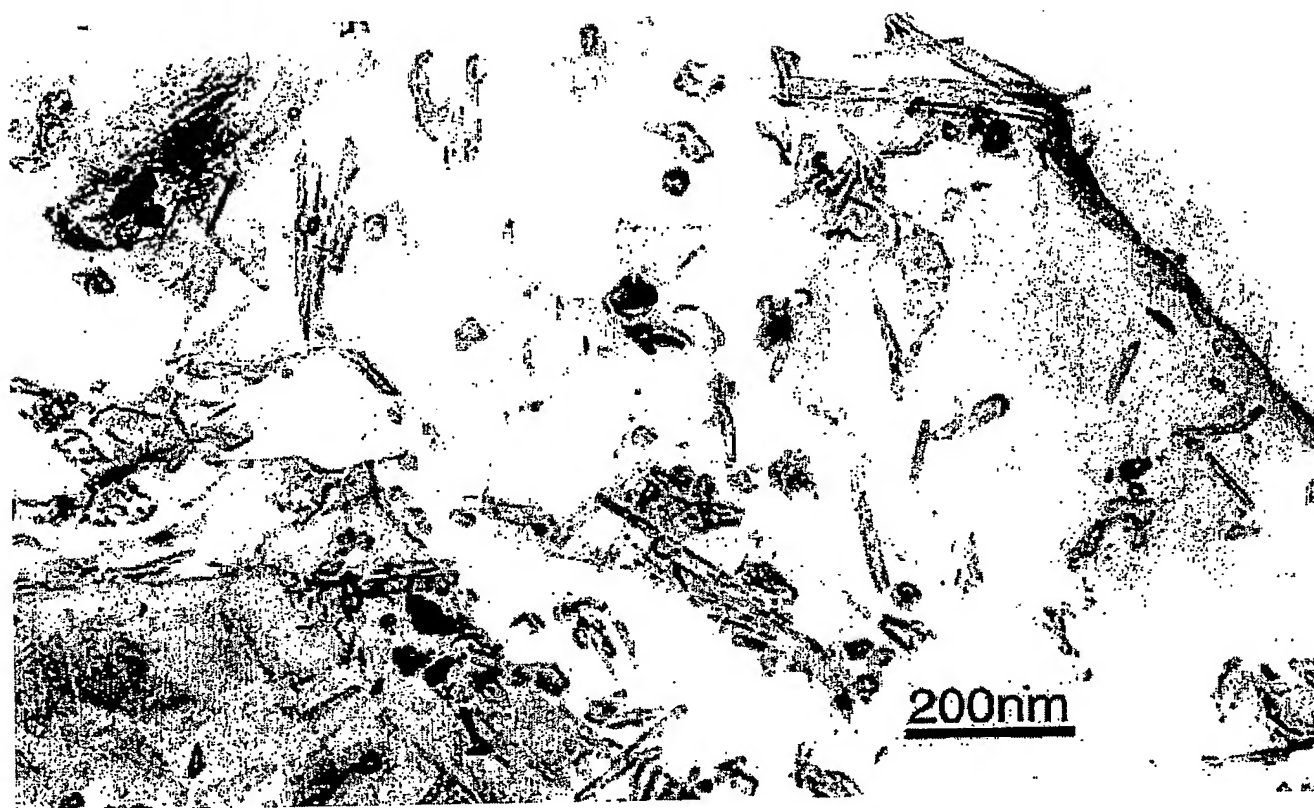


FIG. 11

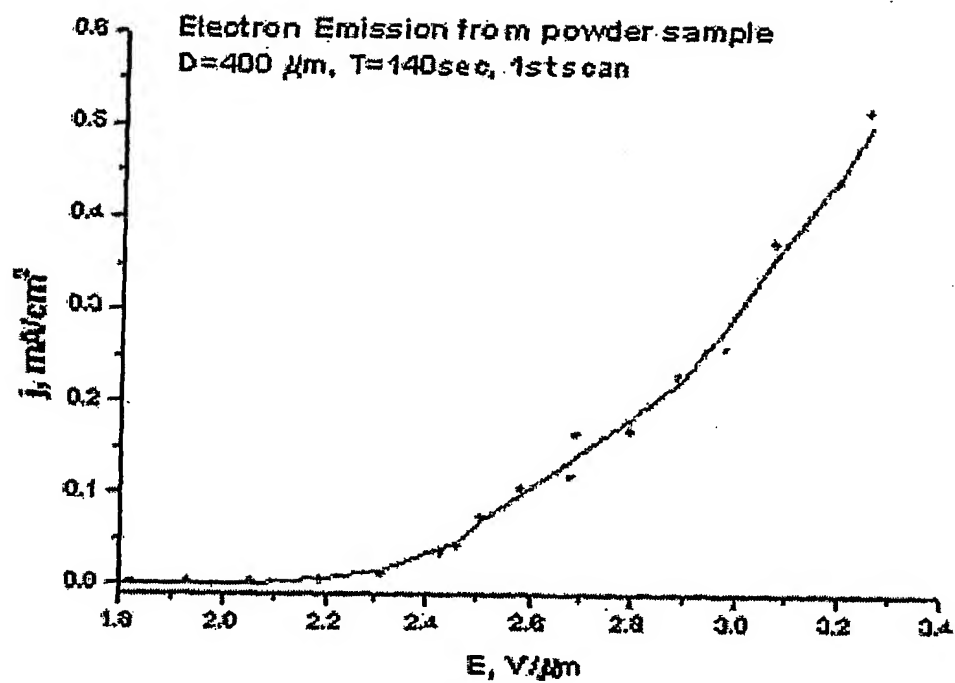


FIG. 12

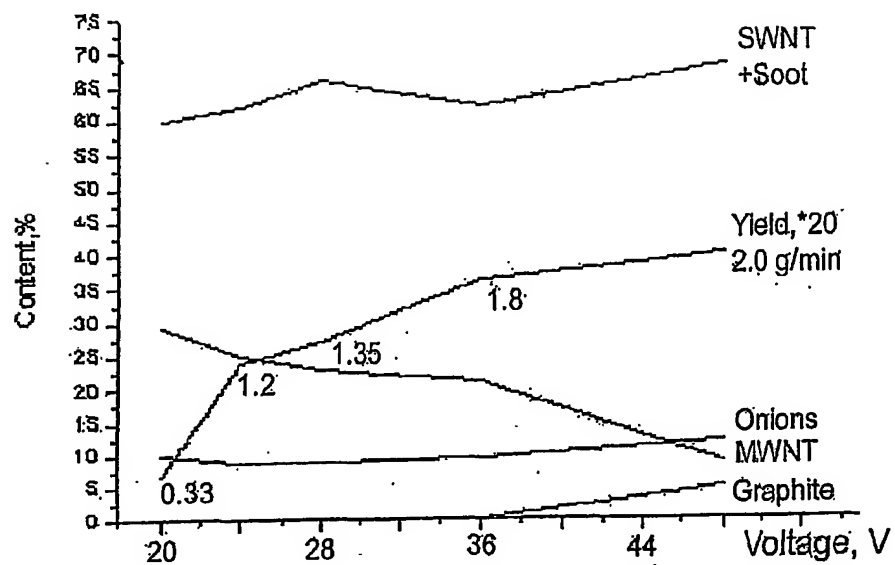


FIG. 14

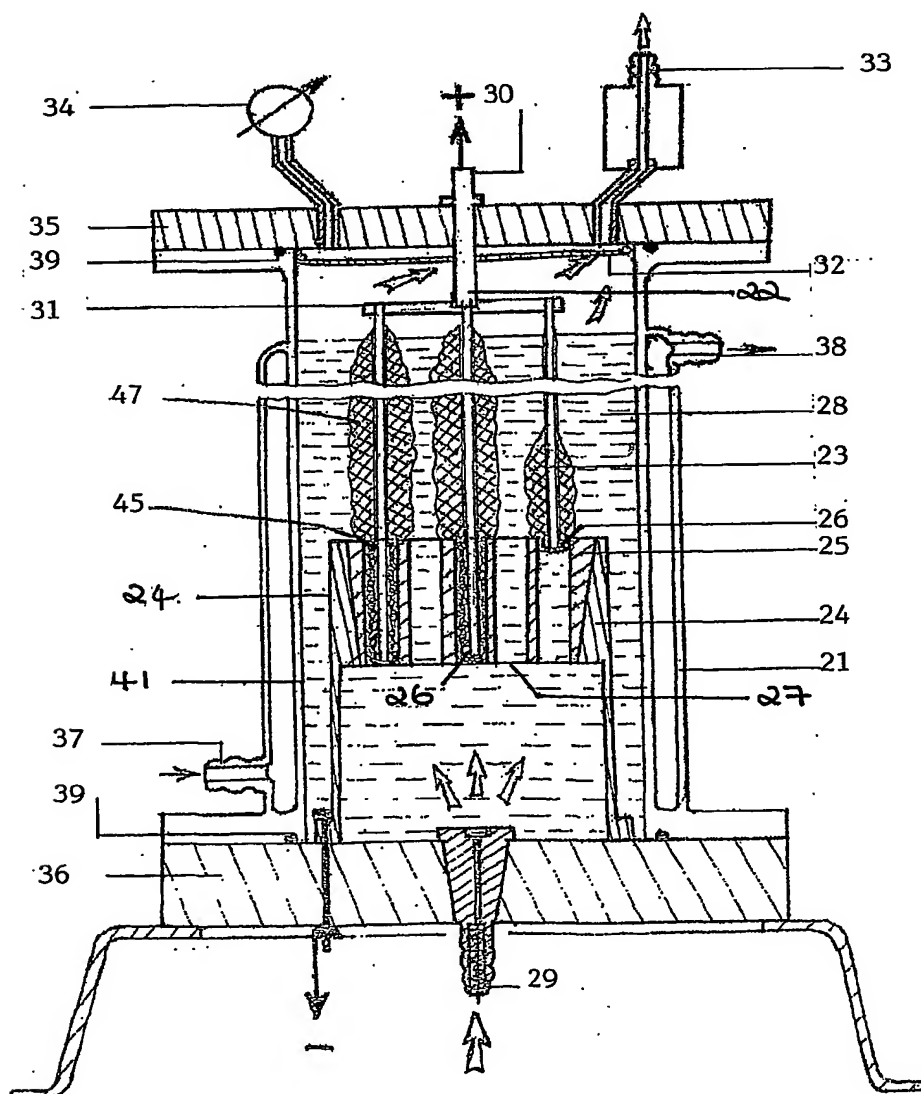


FIG. 13

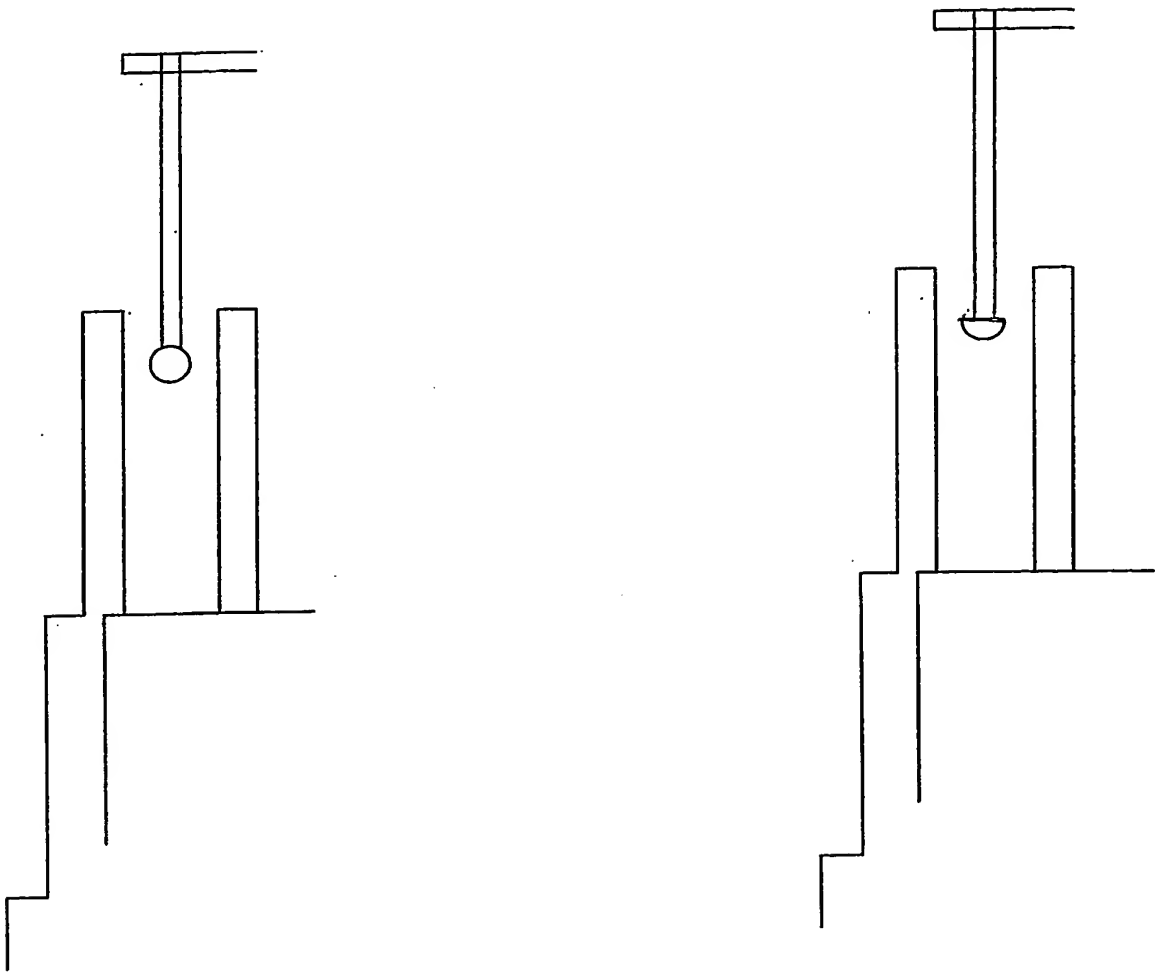
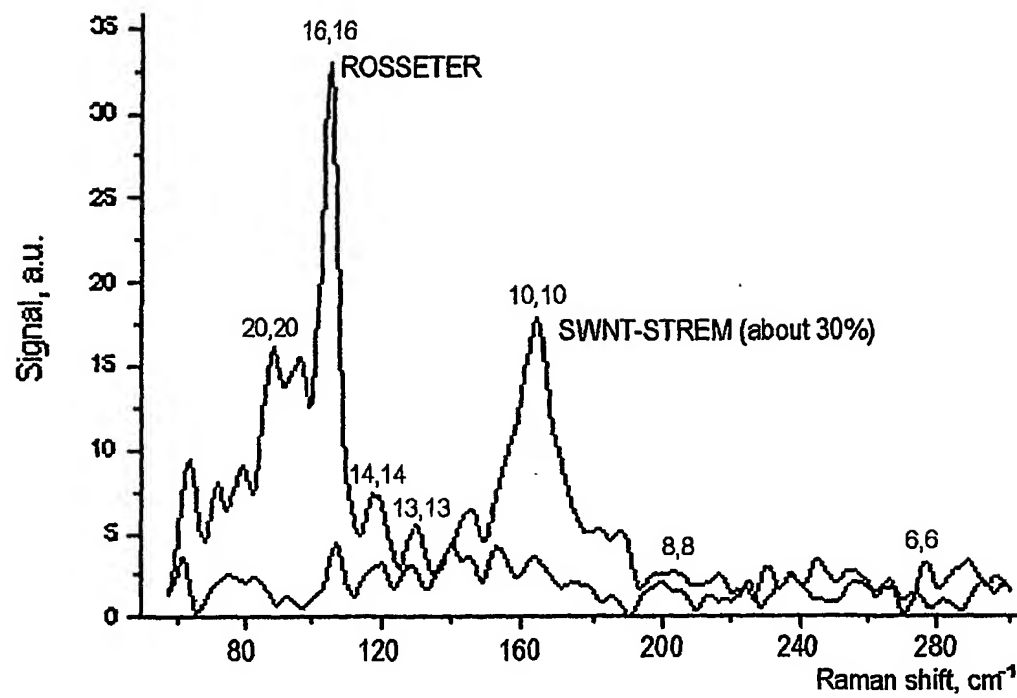
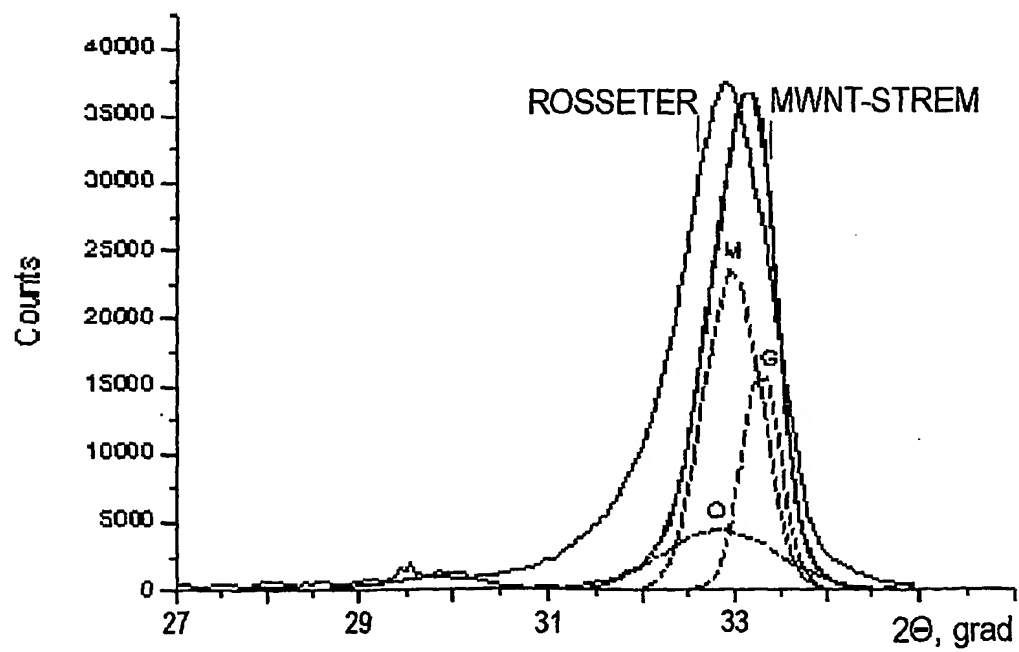
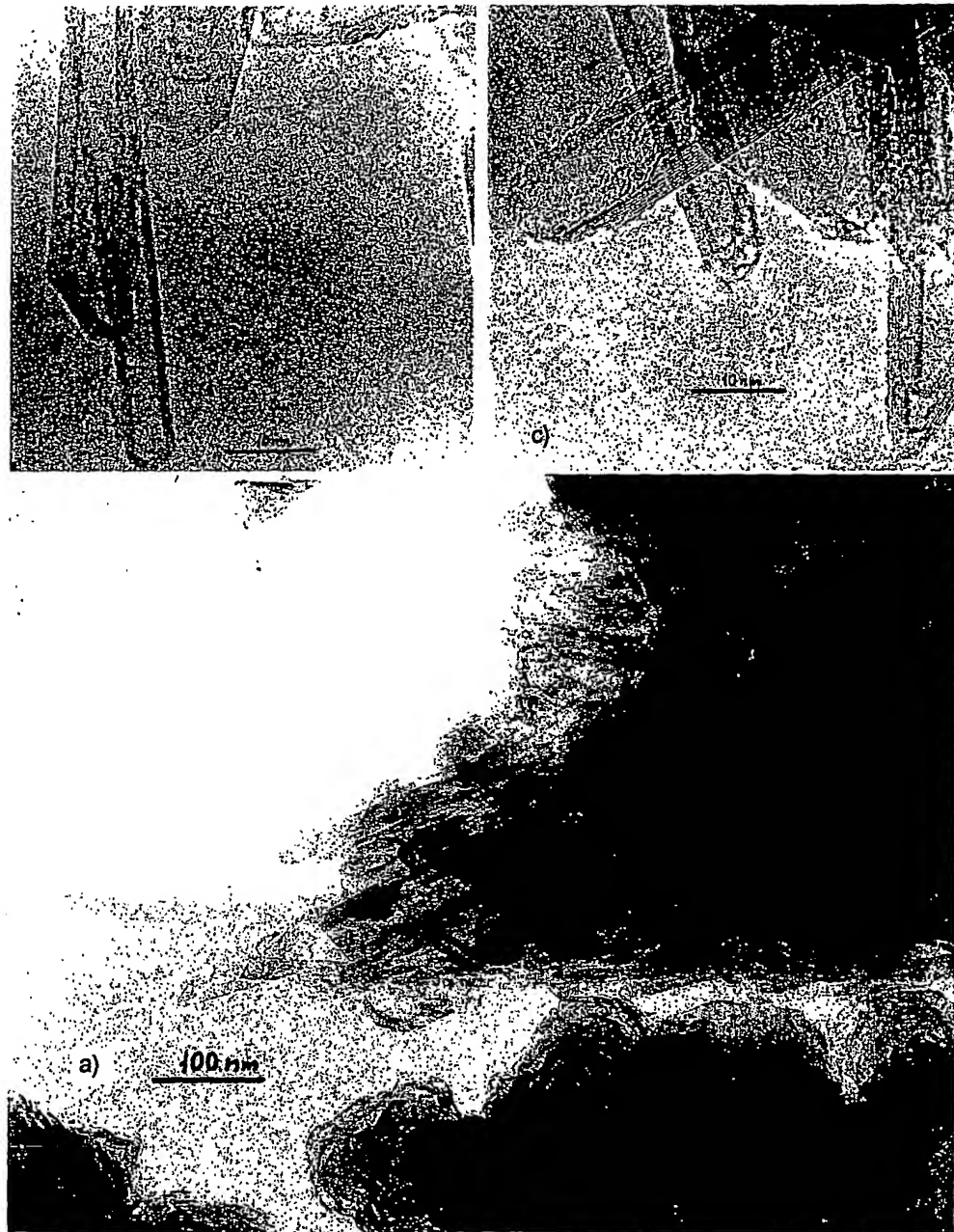


FIG. 15

*Fig. 16**Fig. 17*





*Fig. 18*

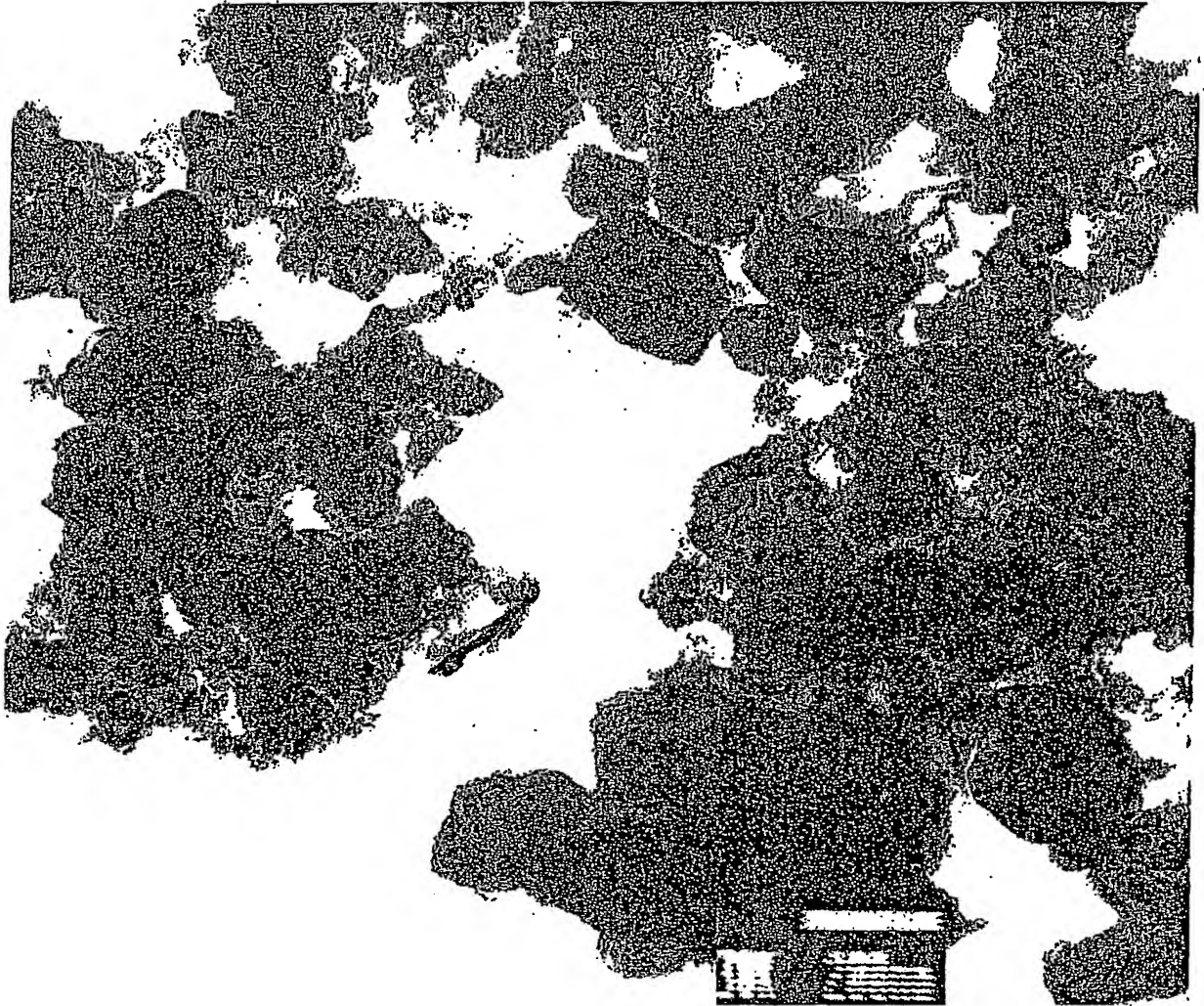


FIG. 19

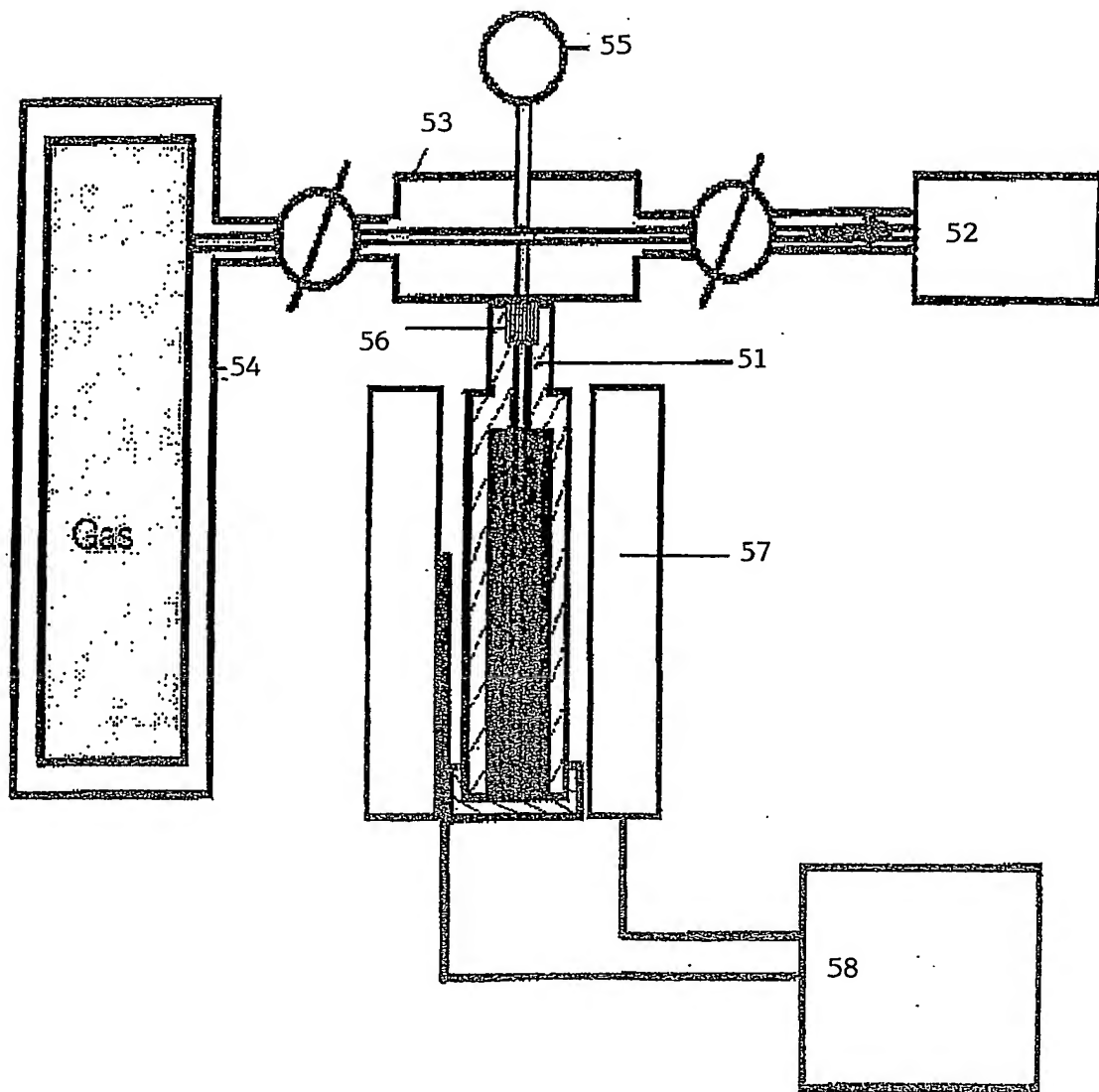


Fig. 20

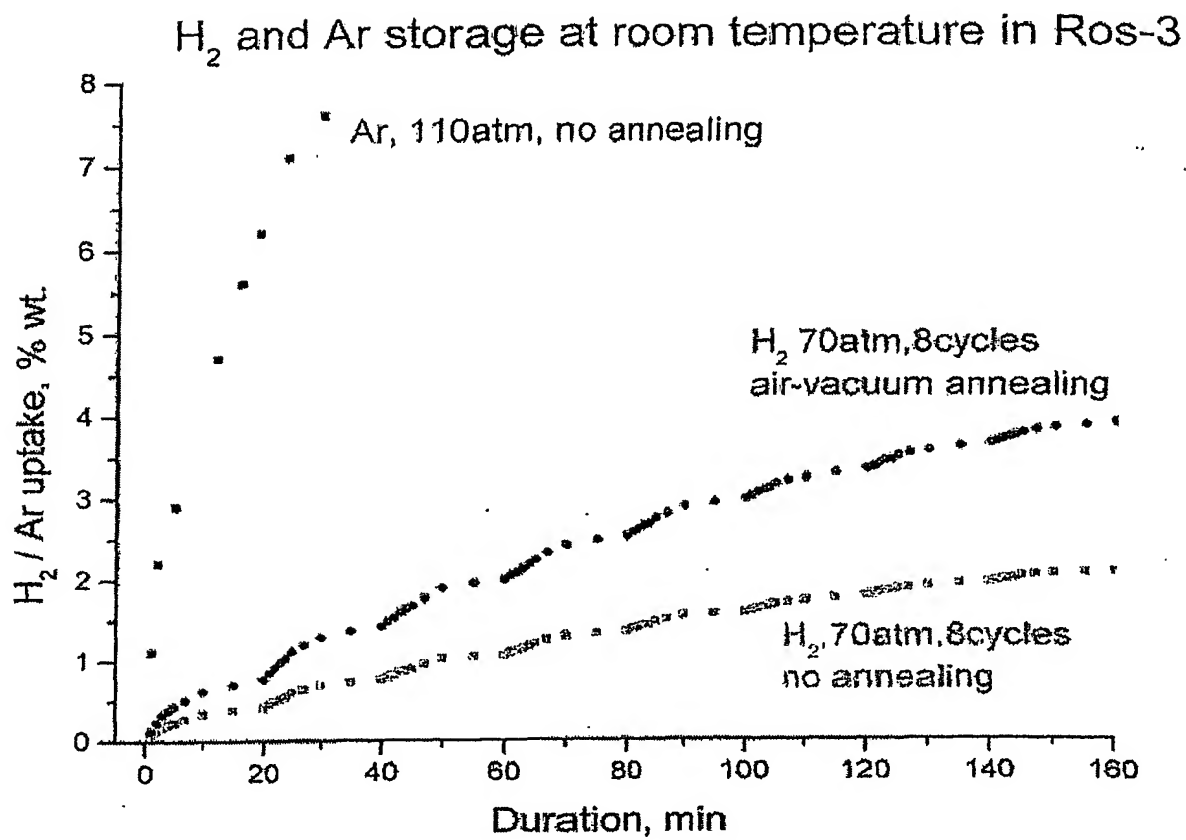


Fig. 21

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
20 March 2003 (20.03.2003)

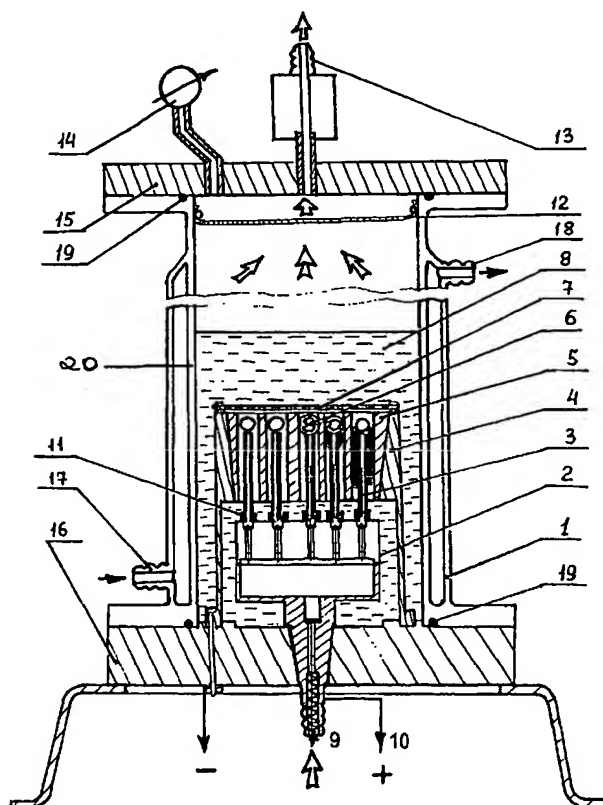
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(10) International Publication Number  
**WO 03/022739 A3**

- (51) International Patent Classification<sup>7</sup>: **C01B 31/02**, **B01J 19/08** (71) Applicant (for all designated States except US): **ROSSETER HOLDINGS LTD [CY/CY]**; 4 Niciforou Lytra, P.O. Box 56860, Limassol 3310 (CY).
- (21) International Application Number: **PCT/GB02/04049** (71) Applicant (for LC only): **OUZMAN, Beverley, Nicola, Claire [GB/GB]**; c/o Murgitroyd & Company, Scotland House, 165-169 Scotland Street, Glasgow G5 8PL (GB).
- (22) International Filing Date:  
6 September 2002 (06.09.2002) (72) Inventor; and
- (25) Filing Language: English (75) Inventor/Applicant (for US only): **RYZHKOV, Vladislav, Andreevitch [RU/CY]**; Kanika Enaerios, Lido 2, Flat 267, Limassol (CY).
- (26) Publication Language: English (74) Agent: **MURGITROYD & COMPANY**; Scotland House, 165-169 Scotland Street, Glasgow G5 8PL (GB).
- (30) Priority Data:  
0121558.1 6 September 2001 (06.09.2001) GB  
0121554.0 6 September 2001 (06.09.2001) GB  
0123491.3 29 September 2001 (29.09.2001) GB  
0123508.4 1 October 2001 (01.10.2001) GB (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,

[Continued on next page]

(54) Title: APPARATUS AND METHOD FOR NANOPARTICLE AND NANOTUBE PRODUCTION, AND USE THEREFOR FOR GAS STORAGE



(57) Abstract: There is provided a method for the enhanced production of fullerenes, nanotubes and nanoparticles. The method relies upon the provision of a hydrocarbon liquid which is converted by a suitable energy source to a synthesis gas such as acetone, ethylene, methane or carbon monoxide, the synthesis gas(es) forming the precursors need for fullerene, nanotube or nanoparticle production. The nanotubes formed by the method described are in general terms shorter and wider than conventionally produced nanotubes. An improved apparatus for production of the fullerenes and nanocarbons is also disclosed wherein a moveable contactor is attached to a first electrode with a sealable chamber, and is spaced from the second electrode such that an electric arc can pass between them.

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GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

- (84) **Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

- (88) **Date of publication of the international search report:**

12 June 2003

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## INTERNATIONAL SEARCH REPORT

 International Application No  
 PCT/GB 02/04049

 A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C01B31/02 B01J19/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

 Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 C01B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, COMPENDEX, CHEM ABS Data, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 61492 A (ROSSETER HOLDINGS LIMITED) 19 October 2000 (2000-10-19) cited in the application page 2, paragraph 7 -page 5, last line ---	1-13, 21-30
X A	US 5 876 684 A (LOUTFY RAOUF O ET AL) 2 March 1999 (1999-03-02) column 6, line 10 - line 49 column 9, line 60 -column 10, line 48; claims 1,5,8; example 9 --- -/--	1-11,13 21-30

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

1 April 2003

Date of mailing of the international search report

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International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MODAK D K ET AL: "A SIMPLE TECHNIQUE FOR PRODUCING FULLERENES FROM ELECTRICALLY DISCHARGED BENZENE AND TOLUENE" INDIAN JOURNAL OF PHYSICS, PART A, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, IN, vol. 67A, no. 4, 1993, pages 307-310, XP000856189 ISSN: 0252-9262 cited in the application page 1 ---	1-8
X	WO 00 14012 A (GALEEV VALERI ;GAMZINE MIKHAIL (CY); FULLTECHNOLOGY LTD (CY); NOVI) 16 March 2000 (2000-03-16) page 2, paragraph 6 -page 5, line 8; figure 1 ---	1, 4-8, 21-24, 30
X	LIU ET AL: "Hydrogen storage in single-walled carbon nanotubes at room temperature" SCIENCE, AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE,, US, vol. 286, no. 5442, 5 November 1999 (1999-11-05), pages 1127-1129, XP002148937 ISSN: 0036-8075 the whole document ---	31-33, 36-40
X	CHENG H M ET AL: "SYNTHESIS AND HYDROGEN STORAGE OF CARBON NANOFIBERS AND SINGLE-WALLED CARBON NANOTUBES" ZEITSCHRIFT FUR METALLKUNDE, DR. RIEDERER VERLAG GMBH. STUTTGART, DE, vol. 91, no. 4, April 2000 (2000-04), pages 306-310, XP000931912 ISSN: 0044-3093 paragraph '0004!; table 1 ---	31, 33, 36-40
X	US 6 090 363 A (GREEN MALCOLM L H ET AL) 18 July 2000 (2000-07-18)	31
A	column 1, line 53 -column 2, line 67; examples 1,2 ---	32-34
X	HIRSCHER M. ET AL: "Hydrogen storage in sonicated carbon materials" APPL. PHYS. A, vol. 72, February 2001 (2001-02), pages 129-132, XP002236718 the whole document ---	31, 32, 37-39
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	-/--	



## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 02/04049

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>GADD G. E.: "The world's smallest gas cylinders?" SCIENCE, vol. 277, 15 August 1997 (1997-08-15), pages 933-936, XP002236719 the whole document -----</p>	31,33, 35-38

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/GB 02/04049

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

-- see additional sheet

As a result of the prior review under R. 40.2(e) PCT,  
part of the additional fees are to be refunded.

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☒ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:  
  
1-13, 21-40
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☒ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-13, 21-30

Method for producing nanocarbon materials like fullerenes, nanotubes or nanoparticles starting from a liquid hydrocarbon and related apparatus.

2. Claims: 14-17

Single walled nanotubes having a diameter of from 2 to 5 nm.

3. Claims: 18-20

Multi walled nanotubes having a mean diameter of from 2 to 15 nm and a length of from 50-1000 nm.

4. Claims: 31-40

Method for inserting a gas in a nanocarbon material and for displacing the afore-mentioned gas with a second gas.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 02/04049

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